THERMAL CONDUCTIVITY OF

REFRACTORY MATERIALS

PUSTOVALOV, V.V.

TRANSLATED FROM RUSSIAN

THERMAL CONDUCTIVITY OF REFRACTORY MATERIALS

(TEPLOPROVODNOST OGNEUPOROV)

PUSTOVALOV, V.V.

Izdatel'stvo "Metallurgiya", 1966

TRANSLATED FROM RUSSIAN

ANNOTATION

The brochure gives a systematic account of methodological problems of determining the thermal conductivity of refractories. The material contained here would help improve experimental techniques, and generalize the factual data required for heat engineering calculations and for solving technological problems associated with refractory science and industry.

The work is meant for engineering, technical and scientific workers of refractory, glass and ceramic industries.

CONTENTS

INTRODUCTION

The study of thermal conductivity of refractory materials continues to remain important even today. This is so, because, generally speaking, the investigations carried out so far applied only to particular cases and were marked by limitation of techniques and by the small number of systematic determinations.

On the other hand, the present state of science and technology in USSR and planned development of national economy have struck out special fields of work in the study of thermal conductivity of refractory materials as a result of the introduction of new materials and the development of industries like thermal insulation, metallurgy, chemical industry, aviation, atomic industry and rocketry. Nowadays, it is practically indispensable to determine the thermal conductivity: (a) of a large variety of refractory materials; (b) of very highly refractory materials such as oxides, zirconates, nitrides and carbides, in a wide range of temperatures (2773-3273 K), right up to the melting point; (c) of refractory materials in vacuum (better than 10^{-4}mm-HgCol) and under high pressures, in protective, regenerative, and oxidizing media, which correspond to the actual operating conditions of many refractories; (d) of refractory materials in the form of powders, readymade materials and special ceramics.

The problems enumerated above form the basis of thermal physics, and involve the study of heat transfer during physico-chemical processes in structural materials at high temperatures [1].

Thermal conductivity is one of the most important physical characteristics of refractory materials. Till recently the data on the thermal conductivity of such materials was so meager that many theoretical aspects of Solid State Physics could not be verified. This can be ascribed to the insufficient study of ther-

i

mal conductivity of refractory materials and to the imperfections in the experimental techniques. Moreover, the laws governing the variation of thermal conductivity as well as the methods of manufacturing refractory materials with given thermo-physical characteristics were not known.

The investigations carried out. essentially related to particular cases. In spite of the large number of published works on the subject [2], compact, accurate and universally useful measuring apparatus were lacking.

Modern science and technology of refractories has still to solve the problems of methodology pertaining to the determination of thermal conductivity and the problems of systematic measurement of thermal conductivity, which are necessary for heat engineering calculations and for solving technological problems of science and technology of refractories.

At present, single-component, single-phase as well as compound, multiphase materials, and dense (even cast) but porous ceramics are being widely used. New materials are being developed. All of them require studies on their thermal conductivity characteristics.

Thermal conductivity measurements of refractory insulators over a wide temperature range, right up to the melting point, yield valuable information for studying the various aspects of thermal conductivity in non-conducting crystals. This is only one of the actual problems of Solid State Physics. Such an experimental study at temperatures above Debye temperature was not possible for quite a long time because of the non-availability of sufficiently pure and dense samples of single crystals and polycrystals and the lack of requisite high temperature techniques.

In the present state of the science and technology of refractories, the production of pure and dense materials would go a long way in formulating accurate methods for determining thermal conductivity. This, in turn, would enable the study of the variation of thermal conductivity with temperature in the case of refractory insulators [3].

While studying the thermal conductivity of refractories, it must be realized that a majority of these materials are

heterogeneous, representing a ceramic or powdery mass containing a large number of pores and empty spaces. Therefore, for an understanding of heat transfer through these materials, it is necessary to determine the factors which influence the effective thermal conductivity over a wide range of temperature.

The present work deals with the following:

1. Study of those laws governing the variations in thermal conductivity of heat insulators, which affect most of the refractory materials.

2. Investigation of parameters which influence the effective thermal conductivity of refractory ceramics.

3. Description of the variety of equipment and experimental methods for determining the variation of thermal conductivity with temperature over a wide range of temperatures, applicable to most of the refractories, viz. heat insulators carbides, graphites, ceramics, and powders.

CHAPTER I

METHODS OF MEASURING THERMAL CONDUCTIVITY OF REFRACTORY MATERIALS

1. Choice of Method

The apparatus available today are not sufficiently developed for tackling all the complicacies met with in the determination of thermal conductivity of refractory materials.

It is therefore worthwhile to develop a system of instru-mentation and techniques with which the thermal conductivity of most of the modern refractory materials can be determined under conditions close to the actual working conditions.

It is clear from a consideration of published works on the determination of thermal conductivity of refractory materials, that out of all the methods, those using a sphere, a cylinder or an ellipsoid under steady state conditions are by large the most accurate, convenient and noncontroversial. Their chief advantage is that the sample, which surrounds the heating source, is also made to "guard" the radial heat flow and so no special precautions are required except those that bring about this condition. But for adopting the methods using the sphere and the ellipsoid [4, 5], very careful preparation of samples is neces-sary and the samples have to be either powders or of complicated shapes. Moreover, it is not possible to study a refractory ceramic or powder at temperatures near its melting point.

From the point of view of sample preparation, the method using a hollow cylinder is more suitable. In this case, there may be errors due to heat exchange through the cylinder ends, but the shape of the samples is much simpler.

This method is based on the measurement of the rate of heat flow under steady state by electrical means. Under this

1

condition, the thermal conductivity is calculated from the formula:

$$\lambda = \frac{\ln \frac{r_1}{r_2}}{2\pi l} \cdot \frac{0.24 \, I \, V}{T_2 - T_1}$$

(1)

where, T_2 = the temperature of the hotter surface of the sample, at radius r_2;

T_1 = the temperature of the colder surface of the sample, at radius r_1;

q = 0.24 I. V = rate of heat flow from the heating element when a current of I (amp) flows under a P. D. of V (volts) through the heating element, along a length l (of the sample).

2. Determination of Thermal Conductivity up to 1773 K (1500°C) in an Atmosphere of Air, Nitrogen, Carbon Dioxide, Argon or other Gases under Pressure and under a Vacuum of 1 x 10^{-4} mm Hg Col

The diagram of the apparatus is shown in Fig. 1. It has a base 1 made of heavy steel disc with a vertical post 2 on which the other parts are mounted. The clamp 4, which can move freely on the post and can be firmly fixed on it, has two semi-circular discs attached to it. The cylinder under test is mounted on one of the discs, while the other disc can be used for preparatory work and, if necessary, it could be used for a simultaneous second experiment with a separate electrical input.

The test shell consists of a centrally mounted sample 13 and two guard blocks 12, 15 on either side of it. The sample as well as the guard blocks are cylinders of 75 mm diameter and 65 mm height with a central hole 19 to 21 mm diameter. In the samples there are two holes for thermocouples (Fig. 2). Channels, instead of holes, can be provided for the sake of simplicity, in materials having thermal conductivity less than 2 kcal/m. h. K (2. 33 watt/m. K).

The dimensions used for the cylinder (height 280 mm, diameter 65 to 75 mm, and a length-to-diameter ratio of 4. 3 to 3. 7) insure a unidimensional cylindrical thermal flux in the central portion of the sample. Such dimensions appear to be optimum, because the thickness of the cylinder is sufficient for setting up
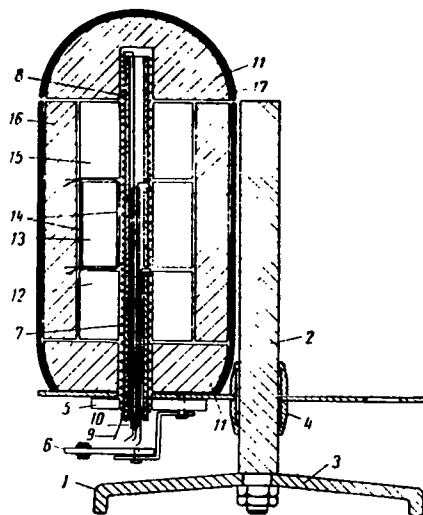
2

Fig. 1. View of an improved apparatus for determining thermal conductivity of refractory materials, which could also be used for refractory powders.

1 - base; 2 - post; 3 - nut fixing the post to the base, 4 - clamp with discs to mount the cylinder under test; 5 - cement asbestos holder for fixing the heating element; 6 - panel with electrical terminals; 7 - tubular former of the heating element; 8 - heating spiral; 9 - potentiometer wires and power leads; 10 - corundum tube; 11 - circular end-insulators; 12 - lower guard; 13 - sample; 14 - thermocouples placed inside the sample to measure the temperature drop; 15 - upper guard; 16 - heat insulation; 17 - asbestos layer.

appreciable temperature drop, even in the case of materials with relatively high thermal conductivity. Moreover, the lengths of the sample and the guards are such that standard bricks could be used without modifying these lengths. The cylindrical casing 16 is made composite to facilitate assembly. It is to be noted that the sample and the guards need not be of the same material. The important requirement is that they should have nearly the same thermal conductivity and about the same temperature coefficient of thermal conductivity. This aspect is especially important in the measurements on materials like fused quartz, fused magnesite, crushed quartzite, whose preparation and working in large quantities is technically difficult. Possible gaps between the ends of the cylinders are eliminated with the help of rings made of asbestos. Asbestos boards prevent heat loss through the ends to a certain extent, while the height of the sample is such that the flow of heat is only radial.
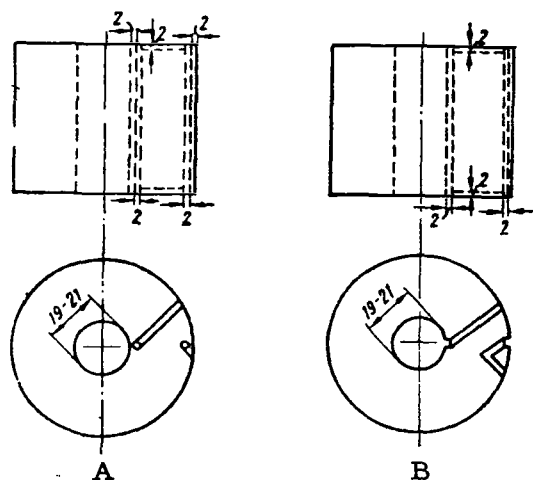
Fig. 2. *Samples for determining thermal conductivity of refractories up to*
1500°C (1773 K).

a - Sample, with holes for thermocouples, suitable for measuring
temperature in materials with thermal conductivity more than
2 kcal/m.h.K.; b - The same as above, with thermocouple channels,
suitable for materials with thermal conductivity less than 2 kcal/m.h.K

At either end of the cylinder, there is a covering of heat
insulating material (e.g., lightweight refractories) protecting the
edges of the heater from which there is a considerable amount of
heat dissipation.

On the outer side, the cylinder is insulated with a 20 mm
thick layer of highly porous, heat-insulating ceramic, consisting
of lightweight Dinas and lightweight firebricks (chamotte) or
better still, ultralight firebricks.

The ultralight material possesses low thermal conducti-
vity (0.1 to 0.2 kcal/m.h.K = 0.16 to 0.23 W/m.K.). It is easy
to machine and has satisfactory strength. A 10 mm coating of
asbestos is given outside the ceramic insulation. This gives
additional strength to the casing half rings and simplifies the
filling of gaps between them.

The casing half rings considerably increase the average
temperature at which the measurements are made. They de-
crease the relevant temperature drops (between hot and cold
faces) in the measurements of thermal conductivity and conse-
quently result in better accuracy of the measurements. The
application of the insulating layer decreases considerably the

power consumption even at very high temperatures and reduces distortion of isothermals on the cold surface of the cylinder due to convection. Nevertheless, the decrease in the temperature drop reduces the accuracy of temperature drop measurement and increases the time required for realizing the steady state condition. The dimensions of the casing are so chosen as to yield the best results.

The other details of the apparatus depend on individual requirements. Two variants of the apparatus have been developed:

1. For measuring the conductivity of highly porous (lightweight) refractories up to 1473 K (1200°C). For this purpose, the apparatus has a through-heating element fixed in two holders which also act as electrical terminals (Fig. 3).

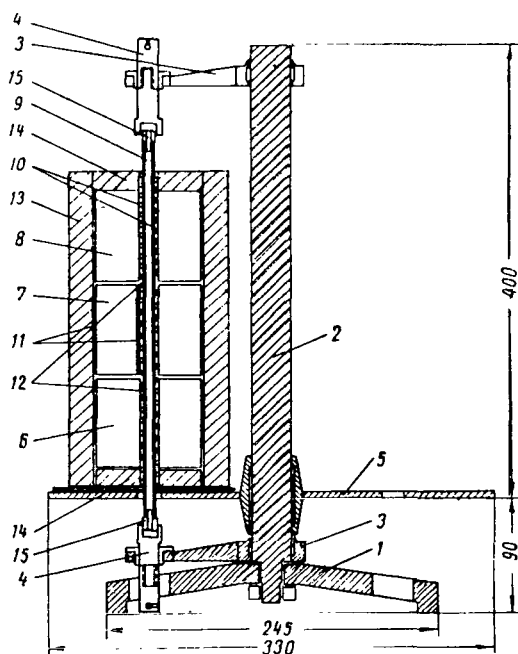Fig. 3. View of the apparatus using through-heating elements with terminals at each end.

1 - base; 2 - post; 3 - electrode holders; 4 - copper electrode;
5 - supporting clamp; 6 - lower guard; 7 - sample; 8 - upper guard;
9 - corundum former of the heater; 10 - heating spiral; 11 - thermo-
couples; 12 - hole for the thermocouple leads; 13 - outer casing;
14 - rings of lightweight ceramic; 15 - copper terminals of the heater.

5

Terminals 15 are of red copper and are insulated by ebonite bushes from the metallic holders soldered to the slide.

The cylinder under test (the sample and the guards) is shown in Fig. 2. The internal hole has a diameter of 13.15 to 14.00 mm. In addition to the central hole, there are channels for thermocouples on the inner and outer surfaces of the cylinder, and channels for thermocouple leads on the end faces. For accurate measurements, a drilled hole to suit the thermocouple is used, instead of the channel (Fig. 2).

Because of simple shape and small dimensions of the sample, it is possible to study not only commercial products, but also experimental samples die-cast in the shape of a cylinder with a central hole. The thermocouple holes and channels are made on samples in the "wet" (unbaked) condition.

2. For measuring thermal conductivity of refractories up to 1773 - 1873 K (1500-1600°C). The apparatus (Fig. 1) has already been described in the previous section. In this case, the central hole is increased to 19 to 21 mm diameter. On the one hand, this facilitates bringing out through one end all the lead wires of the heaters, as well as those for temperature measurement with a minimum of heat loss. On the other hand, it enables the use of the refractory platinum-rhodium wire (for heater), which is not possible in the previous apparatus because of very low resistance of platinum-rhodium.

The heater is uniformly wound on a former which remains sufficiently rigid even at the highest temperatures in use. The former is made of corundum, either by extrusion or when the diameter is large (25-30 mm), by casting in gypsum molds. The required holes are made either in the "green" or in the "initially burnt" tube. Then the body is finally baked till it acquires the minimum porosity.

It is important to insure uniformity in winding the heater wire on the former. This is achieved as follows: two wires, namely, the heating wire, 0.5 to 0.6 mm diameter, (either nichrome, platinum-rhodium, or special alloys) and a secondary wire (nichrome), 0.3 mm diameter, are close wound, touching one another, on the former. After winding the whole length of the former and fixing the heating spiral, the thinner (nichrome) wire is unwound, leaving a uniformly wound heating spiral. The

heater wire is then cemented on to the former with corrax (molten corundum) or with a mixture of well powdered alumina and 10% (by weight) clay or kaolin, in order to get better baking qualities. Such a coating bakes well on to the former and is found suitable for all types of heating elements including those for very high temperatures of 1773-1873 K (1500-1600°C) at the sample, i.e. when the heater temperature is as high as 1873 to 1923 K (1600 to 1650°C).

The cement coating for heating elements of the type with two end terminals (Fig. 4b), which work up to temperatures of 1373 to 1473 K (1100 to 1200°C), can be a mixture of well powdered magnesite burnt to 1873 K (1600°C) and a small quantity of water glass. Although magnesite powder smoothens out temperature variations along the heater length and in between the windings due to its greater thermal conductivity, yet it decomposes at temperatures above 1273 K (1000°C) and reacts with the sample and the heater former.
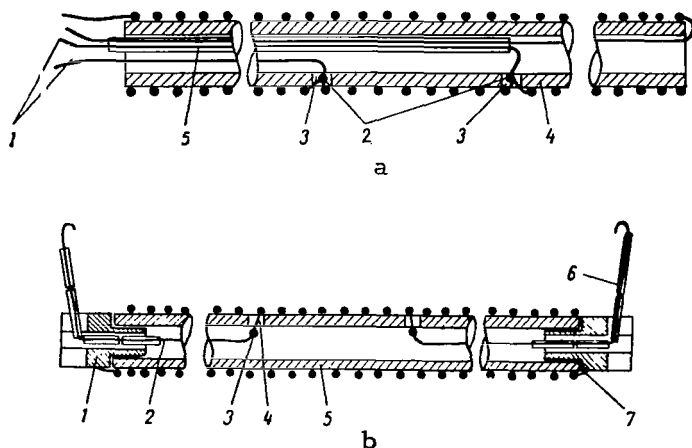
Fig. 4. *Heating elements.*

  a - with single-end feed.

  1 - potentiometer leads; 2 - the points to be welded on to the heating spiral; 3 - hole drilled in the former; 4 - former; 5 - corundum tube.

  b - with two-end contacts.

  1 - heater contacts; 2 - potentiometric leads; 3 - points for welding on to the heating spiral; 4 - hole drilled in the former; 5 - corundum tube; 6 - porcelain insulation; 7 - connection of heating spiral with the contact.

The equipment described above was meant for measuring the heat flow in absolute terms, i.e. the results are not related to reference scales or models. It is therefore important to measure accurately the quantity of heat entering into the sample. In the present case, the quantity of heat flow was measured electrically. The electrical power dissipated in the heater could be a measure of the thermal flux. The current was measured outside the heater. The accuracy of measurement is solely determined by the degree of precision of the measuring instrument. Therefore, the accuracy of power measurement depends on the accuracy of measuring the voltage drop across the length of the sample.

To measure the voltage drop corresponding to the quantity of direct heat flow into the sample, the heater element was made with two holes drilled symmetrically at a distance of 65 to 70 mm in the central portion of the body. In the half-baked stage, the holes were made with an ordinary drill but when they were required to be done on a finished former, they were made with an ultrasonic drilling machine. Through these holes in the former, the heater was connected to potentiometer leads which were also made of the same material (as the heater). In order to get reliable electrical contact, the wires were arc-welded and the weld was covered up in a corundum case.

The potentiometric measurements enabled calculation of the thermal flux to be made in two ways: (1) by computing the power consumed in the whole heater and more accurately, (2) by computing the power consumed in the central portion of the heater. It was then possible to compute the actual specific power.

General view of the two-end heating element made with nichrome or special alloys (alloy 2, EI 626) is shown in Fig. 4b and its single-end version with platinum wires is shown in Fig. 4a. The single-end version enables minimizing the losses through the ends of the cylinder. To avoid short-circuits, two of the three wires are encased in corundum sleeves.

Wire type heaters having potentiometric leads are more difficult to fabricate than the ordinary ones. The heating and the secondary wires are wound in parts: they are first wound up to the first hole, the measuring wire is welded on and then winding is done up to the second hole, where the next measuring wire is welded.

8

The heaters have the following parameters:

1.   The heater with two-end contacts, for temperatures up to 1473 K (1200 °C) at the hot face of the sample (Fig. 4b).

The tubular former of corundum has a length of 300 to 320 mm, outside diameter of 10 mm, inside diameter of 4 to 6 mm, length of the central portion between the holes for the potentiometer leads 70 to 75 mm, heating length of 270 to 280 mm. About 7.5 m nichrome wire of 0.6 mm diameter, resistance 30 to 35 ohms, has been used. The resistance of the alloy of diameter 0.5 mm is about 70 ohms, whereas that of the material EI 626 of diameter 0.5 mm is about 50 ohms. The resistance did not increase appreciably with increase in temperature.

2.   Platinum-rhodium heater (10% Rh) with single-sided feed, for temperatures up to 1773 K (1500-1600 °C) at the hot face (Fig. 4a).

The tubular former of corundum has a length of 300 to 320 mm, outside diameter 15 to 16 mm, internal diameter 10 to 11 mm. The central portion is 70 to 75 mm long. The zero current resistance of the central portion of heater at room temperature is 4.8 ohms, and that of the whole heater 13.8 ohms. Resistance increases rapidly with increase in temperature and becomes 40 to 50 ohms at 1773 K (1500 °C). 14 m of platinum-rhodium wire of 0.5 mm diameter is wound on the heater.

Platinum-rhodium wires with 20 and 40% Rh having a higher melting point (up to 2123 K, i.e., 1850 °C) were also used. But the refractoriness of this wire could not be fully utilized, since the body deformed at temperatures higher than 1873 K (1600°C); moreover, the wire with a higher content of Rh is extremely brittle, which complicates the winding operations and results in pulling up the potentiometer leads, etc. Uniformity of winding and the length l of the central portion were determined by X-ray photography.

The circuit for temperature measurement along with the wiring and instrumentation for power measurement complete the setup for determining the thermal conductivity. The power supply consists of a 1 kw stabilizer transformer supplying 220 V to LATR-1 (power regulator), which feeds the heater. A volt-

9

meter and an ammeter measure the voltage and current in the heater. The voltage drop in the central portion of the heater is recorded by a separate voltmeter. The temperature-measuring circuit consists of thermocouples, their switches and a potentiometer for measuring the thermo-e.m.f.

The cylindrical shell consists of the asbestos sheet, heat insulation rings, the upper and lower guards, the sample and its insulation rings. The alignment of the central holes must be insured while assembling the shell. The heater is placed inside the shell.

The heater is so adjusted with the help of the electrodes that its central portion sits in juxtaposition with the sample. The electrode carriers are fixed to the post and the heater is so clamped to the electrodes that the insulating sleeves and the potentiometer leads rest inside special grooves cut in the electrodes. The springs of the electrodes take up the thermal expansion of the body. After fixing the heater to the electrodes, the cylindrical section is insulated with the two semicircular rings and all gaps and clearances are filled with asbestos.

The preparation for the apparatus with single-sided contacts is simpler. The heater (Fig. 4, a) is firmly fixed in the cement asbestos holder. The assembling is done by lowering the guards, the sample and the cylindrical end insulation on the heater. Thereafter, the composite and shaped case made of heat insulating ceramic is put on. This arrangement reduces the heat losses considerably.

The necessary voltage is approximately set with the voltage regulator. When the temperature of the hotter surface reaches the necessary level and the sample starts getting hot, the voltage is reduced manually till steady state heat flow is established, i.e. the temperatures of the hot and the cold faces do not change any more with a constant power input. Three observations are taken at intervals of 10 minutes each. 4 to 5 values of the thermal conductivity at different temperatures can be determined by this apparatus in 8 to 9 h.

Measurements with Pores of the Material Filled with Different Gases at Atmospheric and Smaller Pressures.

Due to the compact and self-contained nature of the equipment, it could be used without any alteration, for measurements

in vacuum (right up to 1×10^{-4} mm HgCol) as well as under any gaseous atmosphere. For this purpose, the entire assembled apparatus was placed in a standard vacuum chamber of large volume (0.5 m^3). The power leads and the temperature-measuring leads were run along the leads of the vacuum chamber. The air was pumped out of the chamber with rotary and oil diffusion pumps. The rate of air exhaustion was 1000 liters per second.

For taking measurements under a given gaseous atmosphere, the vacuum chamber was emptied to 1×10^{-4} mm HgCol and then filled with the required gas. In spite of the fact that the ceramic released some gas, the large volume of the chamber insured that the necessary atmosphere and the required pressure were sustained for sufficiently long periods. During measurements in vacuum, the heat insulation of the apparatus casing is more effective, since the conductivity of the ceramic is considerably reduced.

Measuring the Effective Thermal Conductivity of Powdered Materials

The abovementioned equipment and method were used for this purpose. However, a hollow cylinder (Fig. 5), filled with the powder under test, was used instead of the cylinder and the casing described previously. The cylinder was made from heat-insulating durable bricks (outer wall) and a corundum tube (inner wall), and asbestos was used as additional external insulation as well as cementing medium. A cover, placed from above, fixed the corundum tube securely. The cylinder was filled with the powder through four openings in the cover. Dimensions of the cylinder were: height 203 mm; outside diameter 91 mm; internal diameter 20.5 mm. Platinum vs platinum-rhodium thermocouples, for measuring the temperature differential, were installed on the inner surface of the cylinder, viz., on the corundum tube and at the ceramic wall. The hot junctions of the thermocouples were situated at the middle of the cylinder height.

The distance between the thermocouple hot junctions was constant and was determined by X-ray photography or by direct measurement. The packing density was calculated from the mass of the powder and the volume of the cylinder. In other respects the method was identical with that for baked refractories.

11
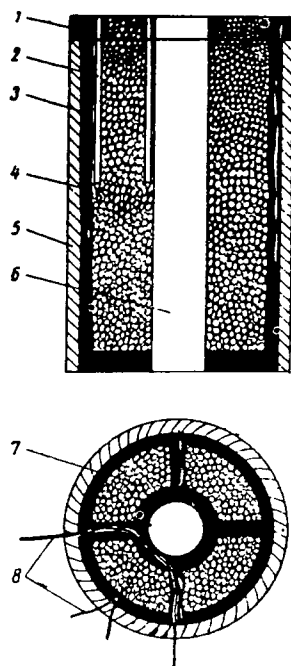
Fig. 5. View of the hollow cylinder, filled with the powder under test.

1 - cover; 2 - corundum sleeve for the thermocouples; 3 - cylinder wall made of lightweight firebrick; 4 - hot junction of the thermocouple; 5 - asbestos insulators; 6 - corundum tube (internal surface of the cylinder); 7 - windows in the cover through which the powder is filled into the cylinder; 8 - thermocouple leads.

The maximum temperature of the measurements was 1473 K (1200°C). At higher temperatures (1300 to 1400°C on the hot face), the smaller particles (less than 0.2 mm) started baking appreciably. Measurements under such conditions were meaningless, because the material behaved as a ceramic rather than as a powder, and the ceramics have heat transfer properties entirely different from those of powders, particularly at lower temperatures (373 to 873 K, i.e. 100 to 600°C).

Errors in the Method

Let us estimate the relative error of the methods described above. In the case of the hollow cylinder, the coefficient of thermal conductivity was determined from equation (1), from which the general expression for the maximum theoretical percentage error is equal to:

12

$$\frac{\Delta\lambda}{\lambda} = \left[\frac{\Delta I}{I} + \frac{\Delta V}{V} + \frac{\Delta T_1 + \Delta T_2}{T_2 - T_1} + \frac{1}{\ln\frac{r_1}{r_2}}\left(\frac{\Delta r_1}{r_1} + \frac{\Delta r_2}{r_2}\right) + \frac{\Delta l}{l}\right] 100\% .$$ (2)

Let us now consider the error contributed separately by each of the terms into the total error.

The precision of the instruments used (voltmeter and ammeter) determines the errors in measuring the voltage and current. In our case the accuracy was 0.5% of full scale deflection. Since the measurements, in our case, were made close to the full scale deflection it can be considered that:

$$\frac{\Delta I}{I} = \pm 0.5\% ; \quad \frac{\Delta V}{V} = \pm 0.5\% .$$

This error is small and the total error introduced by it in heat flow measurements is 1%. However, this error could be reduced by using instruments of higher precision, say 0.2 or even 0.1%. The accuracy of heat flow measurements, due to this, can then be improved to a theoretical value of 0.2-0.4%, which is a small quantity.

The error in determining the radii of points, where thermocouple hot junctions are placed, is at least 0.5 mm, i.e., $\Delta r_1 = \Delta r_2 = 0.5$ mm. (The minimum error is determined by the thickness of the thermocouple wire. For a wire thickness of 0.5 mm and junction thickness of 1 mm, this error cannot be less than 0.5 mm). Lengths were measured by X-ray photography so as to limit Δr to 0.5 mm.

The length of the central portion of the heater and the positions of the thermocouple hot junctions inside the sample, when ready for measuring, were also determined by X-ray photography, which was done on commercially available equipment.

While photographing along the ends of the cylinder, special and sufficiently precise orientation of the end planes perpendicular to the ray axis was necessary. Moreover, in this case, due to the divergence of the rays, a half-shadow was obtained. These shortcomings could be avoided by photographing parallel to the ends. The small contrast at the edges of the hole, due to negligible difference in the thickness of the absorbing layers, could be improved by inserting steel fixtures into the holes while photographing.

The increase in dimensions, obtained due to ray divergence, was determined by means of a reference strip. It is important to consider the increase in dimension for length ℓ only; the ratio of the radii is not affected by the increase.

As a result of all this, the accuracy in estimating the distance, $\Delta\ell$ = 0.5 mm was attained.

For our sample: r_2 = 7.2 to 9.5 mm (average 8.4 mm); r_1 = 35.6 to 38.8 mm (we can take an average of 37.2 mm); $\ln\dfrac{r_1}{r_2}$ = 1.41 to 1.68 (average 1.55); $\Delta\ell$ = 0.5 mm; ℓ = 65 to 75 mm. Substituting these values, the total error due to all the linear measurements seems to be 6.5%. This relatively large amount of error could probably be reduced by using thinner thermocouples (0.2 to 0.3 mm).

The error in temperature measurements depends on many factors --the accuracy of instruments, conformity of the thermocouples to standards, temperatures used for measurement, and conductivity of the material being tested, etc.

Thermo-e.m.f. of the thermocouples was measured with a potentiometer of type PPTV-1 or of type PPTN-1, using a mirror galvanometer of type GZS-47 and standard cells of class 2. This instrumentation had a sensitivity of 0.01 mV, which means that:

$\Delta T_1 = \Delta T_2 = 1^\circ$, for platinum vs platinum-rhodium thermocouples;

$\Delta T_1 = \Delta T_2 = 0.2^\circ$, for chromel-alumel thermocouples;

$\Delta T_1 = \Delta T_2 = 0.1^\circ$, for chromel-coppel thermocouples.

The temperature differentials depend mainly on the conductivity of the material as well as on the temperature, at which they are determined. Typical values of these differentials and the value of the percentage error introduced by them in these experiments on refractories, having the usual values of conductivity, are shown in Tables 1 and 2, respectively.

Obviously, for a given temperature range and for a given conductivity of the sample, suitable thermocouples can be selected so that even at the lowest temperatures of measurement the

TABLE 1

Variation of thermal conductivity of material, with temperature differential ($T_2 - T_1$), at different average temperatures of measurement

Material	Temperature differentials ($T_2 - T_1$) at temperature of measurement, °C, (K)												
	100 (373)	200 (473)	300 (573)	400 (673)	500 (773)	600 (873)	700 (973)	800 (1073)	900 (1173)	1000 (1273)	1100 (1373)	1200 (1473)	1300 (1573)
Magnesite	6.5	17	34	53	75	97	124	148	181	213	258		
Forsterite	17	36	64	92	125	161	195	230	267	308	351	392	
Dinas (Lightweight)	45	73	118	164	213	262	304	355	400				
Firebrick or Chamotte (lightweight)	45	91	138	190	242	293	339	392	432	471	514	552	599

TABLE 2

Percentage errors in measuring temperature drops, with different types of thermocouples, as a function of the test temperature

Refractory	Percentage error $\frac{\Delta T.100}{T_2 - T_1}$ at temperature of measurement, $^{\circ}C$, (K)*												
	100 (373)	200 (473)	300 (573)	400 (673)	500 (773)	600 (873)	700 (973)	800 (1073)	900 (1173)	1000 (1273)	1100 (1373)	1200 (1473)	1300 (1573)
For platinum vs platinum-rhodium thermocouples													
Magnesite	15.4	5.9	2.9	1.9	1.3	1.0	0.8	0.7	0.6	0.5	0.4		
Forsterite	5.9	2.8	1.6	1.1	0.9	0.6	0.5	0.4	0.4	0.3	0.3		
Dinas (lightweight)	2.2	1.4	0.8	0.6	0.5	0.4	0.3	0.3	0.3				
Firebrick (light-weight)	2.2	1.1	0.7	0.5	0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2
For chromel vs alumel thermocouples													
Magnesite	3.1	1.2	0.6	0.4	0.3	0.2	0.2	0.1	0.1				
Forsterite	1.5.	0.6	0.3	0.2	0.2	0.1	0.1	0.1	0.1				
Dinas (lightweight)	0.4	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1				
Firebrick (light-weight)	- 0.4	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1				

*For chromel vs. coppel thermocouples, the percentage error is half that for chromel vs alumel.

accuracy in measuring the differential may not be less than 3%. With increase in temperature, this error decreases rapidly.

Therefore we have, for errors in temperature measurement, the following:

Temperature, K (°C)	%
373 (100)	3.1
573 (300)	0.6
773 (500)	0.3
973 (700)	0.2
1173 (900)	0.1

Summing up all the errors, we have:

Temperature, K (°C)	%
373 (100)	10.6
573 (300)	8.1
773 (500)	7.8
973 (700)	7.7
1173 (900)	7.6

In this method, the major portion of the error is due to errors in linear measurements; the other errors are comparatively small.

Errors in linear measurements are also significant in the ellipsoid and hollow cylinder methods because the distance between the thermocouple junctions is only 10 mm. However, some authors [26, 4, 5], do not include the error due to linear measurements in the total errors while stating their errors.

In the abovementioned method, there is another fundamental difference compared to the American shell methods, viz. that the thermocouple wires traverse an isothermal zone and this reduces the heat conduction through them. Repeatability of the results was verified in the case of Dinas. The mean square deviation for the whole of the temperature range is 8%.

Verification of the Heat Losses Along the Heat Flow Direction

This heat dissipation in the hollow cylinder method is considerably less as compared to that in the flat plate method, due to the shape of the sample and the heater. (In the case of the hollow sphere and the hollow ellipsoid, the heat losses are completely eliminated). Keeping the length-to-diameter ratio of 4:1 to 3:1 for the cylinder, the heat losses were studied in the case of the two-end heater type apparatus.

One of the methods for this consists in placing thermocouples on the upper and lower guard blocks, in positions corresponding to the thermocouples on the hot and cold faces of the sample. Experiments were conducted on lightweight Dinas, whose thermal insulation properties are such that they can only enhance the sideway heat losses. In other words, the experimental conditions were more rigid than met with in practice. Results of experiments are shown in Table 3.

TABLE 3

Distribution of temperatures on the cylinder under test, ^{o}C

Hot face			Cold face		
Sample (r=8.5 mm)	Upper guard (r=7.7 mm)	Lower guard (r=7.8 mm)	Sample (r=37.4 mm)	Upper guard (r=35.4 mm)	Lower guard (r=37.4 mm)
113	115	125	77	70	74
199	218	227	127	116	121
302	346	355	188	165	169
410	425	424	239	208	215
501	515	514	290	303	312
603	624	618	392	352	362
701	729	722	450	401	413
800	815	813	496	439	455
899	913	915			

It is seen that at the first thermocouple near the hot face, there is practically no variation of temperature along the whole length of the cylinder (i.e., over a length 2ℓ) provided the nonuniformity of cylinder radius r is taken into account.

The temperature of the cold face however, varies to a certain extent (along the length), mainly because of the heat losses. At a hot face temperature of 1073 K (800°C), the temperature drop over the length ℓ is 47°C, while the radial temperature drop is 400°C. And, considering the nonuniformity of the sectional areas, the heat losses amount to only 2%.

$$Q' = \frac{\lambda(T_2' - T_1')}{\ln \frac{r_1}{r_2}} \cdot 2\pi\ell, \text{ for the main radial heat flow} \tag{3}$$

$$Q = \frac{\lambda(T_2 - T_1)S}{\ell}, \quad \text{for losses through the ends} \tag{4}$$

In our case $T_2' - T_1' \approx 400°$; $1 = 65$ mm; $T_2 - T_1 \approx 47°$; $S = \frac{\pi}{4}(75^2 - 10^2)$,

therefore,

$$\frac{Q}{Q'} = \frac{T_2 - T_1}{T_2' - T_1'} \cdot \frac{2\pi\ell^2}{S} \approx 52.$$

The heat flow losses account for 2%. This is close to the value computed on the basis of power consumption in various sections of the heater; in fact, it is less than that. This is so, because we have considered only a part of the cylinder.

Experiments with samples of different heights give a definite confirmation of the negligible heat losses through ends, during precise determinations of thermal conductivity.

Results of measurements on samples of 65 mm height (corresponding to the height of commercial refractory) and 35 mm height are shown in Fig.6. The reduction in height of the sample in the second case was compensated by increasing the height of the guards.

The experimental results show that the values of the thermal conductivity, determined on samples of different heights, are the same within the limits of errors of measurement. In addition, verification was done on three types of refractory ceramics differing greatly from one another in conductivity and temperature characteristics. Moreover, the results of experiments on models of different heights indicate the possibility of
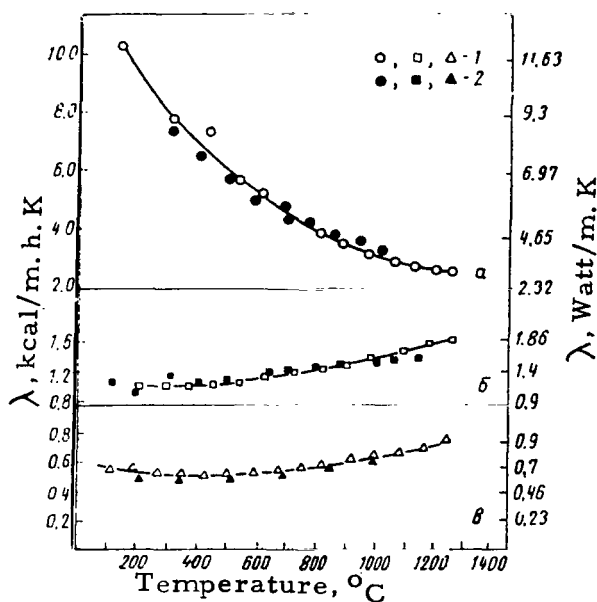
Fig. 6. *Verification of the possibility of reducing sample height.*
a - "Satkin" magnesite, i.e., magnesite from Satkin; b - Dinas;
c - light forsterite.
1 - samples of 65 mm height; 2 - samples of 35 mm height

conducting tests on small size samples of materials which are in short supply or difficult to manufacture.

Qualitative checks, made by several methods, on the heat losses in the apparatus with a two-end heater show, that heat dissipation due to radial flow accounts for not more than 8% and under better insulation conditions it is practically nil. Moreover, such end losses do not affect the conductivity measurements.

In the improved apparatus (Fig. 1) the losses through the ends are so small that they can be neglected.

While developing the apparatus, it was important to compare the results obtained by the method with other known methods on known materials, which are usually taken as reference materials. The choice of a refractory insulator, as a reference material is difficult due to technical difficulties in getting very pure non-ceramic samples. A comparatively good material is quartz glass, which is free from at least one defect, namely, the presence of pores.

20

The results of previously published works [27 to 29] were grouped together [27] to draw an averaged curve (Fig. 7, curve 1) for fused transparent quartz, in which the accuracy of measurement was ± 10 to 12%.

Thermal conductivity measurements of quartz glass in the present apparatus gave a temperature-thermal conductivity curve (Fig. 7, curve 2), which is somewhat lower than the published values [27] mentioned above, but the accuracy of measurement was +8%. In the middle of the temperature range (700 to 1000 K), the difference between the two curves lies within the limits of accuracy of the curves. At the beginning and at the end of the curves, the disagreement is more than the total experimental error. It must be noted that quartz used for experiments was cut out from big blocks which had a fairly large amount of impurity. This could have caused the disagreement in the results, especially at more than 1000 K.
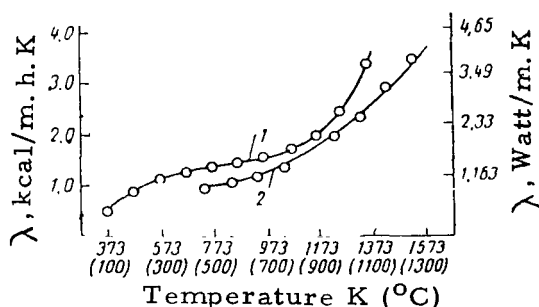

Fig. 7. Comparison of data on thermal conductivity of quartz glass.
1 - averaged curve as per published data [27-29]; 2 - the curve from the author's data.

It should be noted, however, that even with the errors mentioned above and the differences in purity of the samples, the tests show that the apparatus and the experimental method are sufficiently reliable.

Thermocouple Positions Inside the Sample

The thermocouples on the sample are situated near the outer and the inner surfaces of the cylinder. They can be placed either in channels cut along the cylinder surfaces and covered with a mixture of powdered alumina or they can be put in holes, 1.5 to 2 mm diameter, drilled at a distance of 1 to 3 mm from the surfaces.

21

The junctions are kept at the center line of the sample. For measurements in materials with thermal conductivity of 1 to 2 kcal/m. h. K (1. 16 to 2. 33 watt/m. °C), any other convenient way of fixing the thermocouples in channels can be resorted to. For more conducting samples and for precise measurements, the thermocouples should be placed inside holes, because the temperature distribution around couples, especially at the hotter junction, gets disturbed by filling with alumina or even by the sample material itself. The distortion in temperature distribution is most noticeable while working in vacuum, where the loosely baked filler material acts as an additional thermal resistance.

The thermocouple hole is filled with a fine powder of the sample material. An increase in the hole size beyond 1. 5 to 2 mm leads to uncertainty of the position of the junction and it is possible that it may not touch the wall of the hole.

Main characteristics of the apparatus described above are:

a.　possibility of measuring in practically any atmosphere (air, vacuum, or special atmospheres);

b.　possibility of testing specimens of commercial products (without placing limitations on grain, porosity and other technological factors) and also laboratory samples;

c.　relatively small size of sample facilitates experiments on short-supply and expensive samples. Besides this, the geometry of the sample is simple;

d.　small dimensions of the apparatus and consequently smaller time constant;

e.　a wide range of temperatures: 373 to 1773 K (100 to 1500°C);

f.　possibility of measuring thermal conductivity from very low values (0. 2 kcal/m. h. K, i. e., 0. 23 watt/m. °C) to relatively high values (10 to 20 kcal/m. h. K, i. e., 11. 63 to 23. 3 watt/m. °C);

g.　satisfactory accuracy of measurements, good reproductibility and low thermal losses. The choice of one of the

steady state heat flow methods makes the apparatus as a whole simple and the computation of thermal conductivity also becomes simple;

h.   low time constant of the apparatus enables 4 to 5 conductivity measurements at various temperatures in 8 to 9 h. The number of observations reduce to 3 to 4 for heat insulators, particularly in the case of determination of the effective value of thermal conductivity of powders, due to the slow heating up.

Because of the simple construction and easy availability of the requisite instruments, and because of the simple measuring procedure, the apparatus has been widely used in many scientific and technical research works. It has been more particularly used for the control of thermal conductivity value in the manufacture of light refractories and for studying the thermal conductivity of hard compounds of refractory oxides.

3. Special Methods for Determining Thermal Conductivity

The abovementioned apparatus and the measurement technique for determining thermal conductivity could be utilized for various special investigations, such as measurements in vacuum up to 1973 K (1700 °C) and simplified measurements up to 1773 K (1500°C), as well as for studying thermal insulating properties of refractory ceramics. The necessary modifications of the apparatus for these cases are briefly discussed below.

The Comparator Method for Determining Thermal Conductivity

The cylindrical shell (outside diameter up to 100 mm, internal diameter 14 mm), consisting of the sample 6, symmetrical guards 4 and heat insulating rings 3, is fixed on the metal base 10 of the apparatus (Fig. 8). The guards, having a thermal conductivity close to that of the sample and the lightweight insulation rings, are meant for reducing the heat losses along the axis of the apparatus. A standard carborundum heater 320 mm long and 12 mm diameter 5 is fixed inside the cylinder on centering spring clamps. The clamps are insulated from the body and are cooled with flowing water. The sample is cylindrical, 65 to 70 mm high and up to 100 mm diameter. A through-hole

14 mm diameter is drilled in the center of the sample to hold the heater and there are three holes for the thermocouples 11.
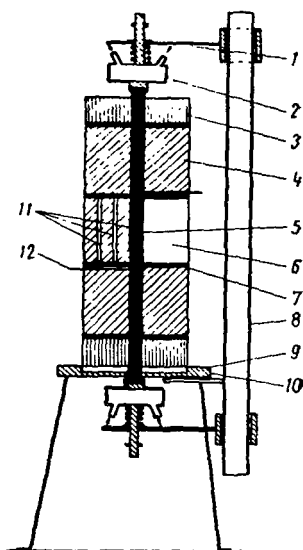

Fig. 8. View of the apparatus for measurement of absolute thermal conducti-
vity by comparison method.
1 - electrode holder; 2 - air cooled electrode; 3 - rings of lightweight insulation; 4 - guard; 5 - heater; 6 - sample; 7 - powdered alumina layer; 8 - fixing column; 9 - cement asbestos; 10 - base; 11 - thermo-couples; 12 - probe.

Temperature is measured with platinum vs platinum-rhodium thermocouples. For colder surfaces, chromel-alumel thermocouples may be used.

While determining thermal conductivity with this apparatus, the annular layer along the whole length of the sample between the third and second thermocouples (T_3, T_2) is taken as the material under test. The layer between the second and first (T_2, T_1) thermocouples is taken as the reference material of known thermal conductivity.

Then, the thermal conductivity ($\lambda_{T_3 - T_2}$) of the material, at the high temperature layer ($T_3 - T_2$), is expressed in terms of the conductivity ($\lambda_{T_2 - T_1}$) of the reference layer ($T_2 - T_1$), as follows:

$$\lambda_{T_3} - T_2 = \frac{\ln \frac{\hbar_2}{\hbar_3}}{\ln \frac{\hbar_1}{\hbar_2}} \cdot \lambda_2 - T_1 \cdot \frac{T_2 - T_1}{T_3 - T_2} \quad (5)$$

24

where T_3, T_2, T_1 are the temperatures at radii r_3, r_2, r_1, respectively. (The temperatures are measured with thermo-couples and distances between them are measured either by X-ray photography or by direct measurement).

The low temperature (up to 1273 K) thermal conductivity value of the sample, used for calculating the required thermal conductivity while testing with carborundum heater (up to 1773 K), is determined on the same sample and with the same test cylinder as in the absolute method*, using the nichrome heater described before.

An attempt was also made to measure absolute thermal conductivity by means of the heat input of the sample heated with carborundum heater. For this purpose, the voltage drop was measured under steady state conditions, in the central por-tion of the heater, by a momemtary contact of steel pins (probes) connected to a voltmeter. The measured variation of thermal conductivity of a zirconium dioxide sample is shown in Fig. 9.
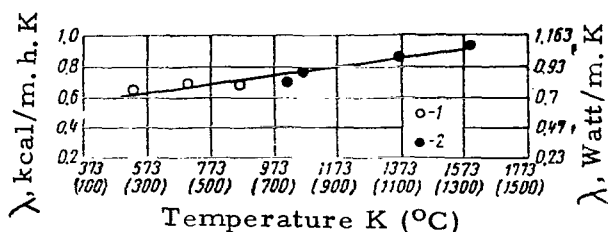

Fig. 9. *Absolute thermal conductivity vs temperature relationship for zirco-nium dioxide, determined by the comparator method.*
1 - by absolute measurement and 2 - by comparison method.

While making the measurements on forsterite, the scatter-ing of experimental points did not exceed 7% at the hot face tem-perature of 873 K (600 °C), 3% at 1573 K (1300 °C) and 1% at 1673 K (1400 °C).

Comparison of the data obtained for thermal conductivity of magnesite-chromium sample by this apparatus, with the data of A. F. Kolechkova and V. V. Goncharov [39] on the same

The terms "absolute method" and "absolute thermal conductivity" are used to indicate that the measurement does not require a reference material.

material, shows that the maximum divergence in the results at high temperatures falls within the limits of accuracy of the method.

The method is slightly cumbersome, but it enables to obtain the temperature-conductivity relationship up to high temperatures, i.e. up to 1773 K (1500 °C) by using the widely used carborundum heating elements and nichrome wire, thereby avoiding the platinum-rhodium wire which is in short supply.

Determining Thermal Conductivity up to 1973 K (1700°C), in Vacuum

Measurement of conductivity above 1773 K (1500°C) was not possible in the apparatus described in Section 2, because of the unavailability of high temperature heater wires which could satisfactorily work in vacuum. Since tungsten and molybdenum could be used as heating wires in vacuum, a modification of the apparatus to measure up to 1973 K (1700°C) was possible.

The following changes were made to suit the measurements in vacuum: 1. The asbestos-covered lightweight refractory insulation layer was replaced by a more insulating layer of light refractory material having high alumina content (the asbestos was replaced because of copious gas occlusion at high temperatures); 2. Water-cooling was dispensed with, heavier copper electrodes were used and the copper contacts for the heater were replaced by graphite; 3. Tungsten and molybdenum were used as heating wires. The parameters of typical heating elements are given in Table 4.

During the measurements, the apparatus, with the heater fixed inside it, was placed in a 0.5 m³ vacuum chamber and the power supply lines and measuring wires were led through the vacuum inlet. To conduct measurements up to the highest temperatures, the more powerful autotransformer type RNO-250-10 was used instead of type RNO-250-2.

It was not possible to weld the potentiometer leads to the tungsten and molybdenum wires and to keep the junction inside a sleeve, because of frequent breakage of the junction. The voltage drop was therefore measured at the ends of the heater.

TABLE 4

Special high temperature heaters for measuring thermal con-
ductivity in vacuum

Parameters	Heaters	
	1*	2**
Former (corundum tube):		
length, mm	377	380
outside diameter, mm	18	25
Molybdenum wire:		
length of heating section, mm	257	257
wire size, mm	0.5	0.8
No. of turns	155	211***
Approximate wire length; m	11	17
Electrical resistance, ohms:		
when cold	3.4	1.97
at 773 K (500°C) on hot face	11.6	7.1
at 1873 K (1600°C)	26.2	-
at 1973 K (1700°C)	-	17.0

* A temperature of 1903 K (1630°C) was obtained on the sample at a current of 7.2 amp and a voltage of 189 v.

** A temperature of 1968 K (1695°C) was obtained at 11.8 amp and 200 v.

*** distance between the turns, 0.4 mm.

The hollow cylinder under test consisted of seven pairs of
semi-circular rings, the middle pair being the sample (Fig. 10).
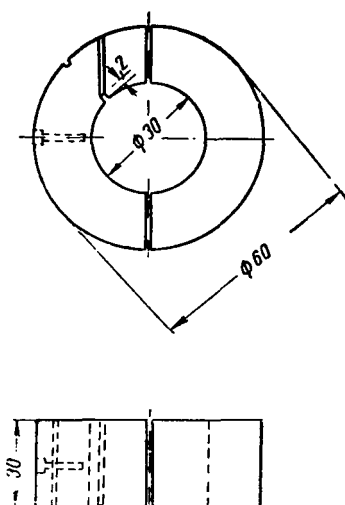In the "green" sample, channels were cut for thermocouples

Fig. 10. *The sample for in vacuo measurement up to a temperature of 1700°C.*

(platinum vs. platinum-rhodium, or tungsten vs. molybdenum-
aluminum) and a shaped passage was provided for the pyro-
meter leads for measuring the temperature gradient. The
thermocouple positions and all the required distances were
determined either by X-ray photography or, with lesser accu-
racy, by direct measurements. The heat input power was
computed from the current and the voltage drop.

The thermal conductivity-temperature relationship of
several refractory oxides, in pure condition, was determined,
at high temperatures in vacuum, by the modified apparatus.

The samples were prepared by pressing and then burning
off the binder material. Measurements up to 1973 K (1700°C),
using the wire heater, were found extremely accurate because
of the negligible end losses. It is to be noted that in vacuum,
each contact surface between the half rings has a very high
thermal resistance, due to which heat losses from the ends
become much less in vacuum than otherwise.

The simplicity of measurement and the high accuracy obtainable make the wire heater method suitable for measuring thermal conductivity of pure oxide materials (zirconium dioxide, aluminum oxide, magnesium oxide, etc.) under vacuum, up to 1973 K (1700°C). Temperatures more than 1973 K (1700°C) at the hot face of zirconium dioxide or alumina samples could not be obtained, because the corundum former fused and also underwent deformation under its own weight. For more conducting materials (graphites, carbides, nitrides, borides), a temperature of only 1673 K (1400°C) could be obtained at the hot face by using the wire heaters.

The miniature apparatus (Fig. 11) (with dimensions of the sample: 65 mm high, outside diameter 30 to 35 mm, internal diameter 10 to 10.5 mm and length-diameter ratio of 2:1) is a variation of the apparatus described above. The small length to diameter ratio is compensated by thermal end insulation.
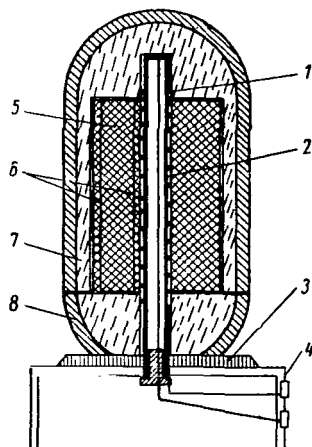

Fig. 11. Apparatus of small dimensions for determining thermal conductivity of small samples.
1 - tubular former; 2 - heating wire; 3 - asbestos cement packing; 4 - base; 5 - sample; 6 - thermocouples; 7 - refractory ceramic insulation layer; 8 - asbestos layer.

The thermal conductivity values of an extremely light refractory and of commercial forsterite, measured on the miniature apparatus, do not differ from those determined on the standard apparatus within the limits of experimental errors (Table 5). Such a miniature apparatus could be used for qualitative measurement of thermal conductivity for the quality control of heat insulating refractories.

TABLE 5

Thermal conductivity of an extremely light refractory material and on
commercial forsterite

Extremely light refractory		Forsterite			
$T_{average}$	λ, kcal/m.h.K (Watt/m. ^{o}C)	$T_{average}$	λ, kcal/m.h.K (Watt/m. ^{o}C)	$T_{average}$	λ kcal/m.h.K (Watt/m. ^{o}C)
125	0.19 (0.22)	87	2.52 (2.93)	737	1.6 (1.86)
230	0.17 (0.19)	275	1.76 (2.05)	796	1.6 (1.86)
395	0.19 (0.22)	308	2.06 (2.4)	847	1.54 (1.79)
505	0.20 (0.23)	392	2.01 (2.34)	960	1.56 (1.82)
655	0.23 (0.27)	465	1.92 (2.22)	-	-
790	0.25 (0.29)				

4. Measuring Thermal Conductivity up to the Melting Points of Highly Refractory materials -- 2673 K (2400°C)

The contents of Sections 2 and 3 were taken into considera-
tion while choosing the method and design of apparatus for evolv-
ing a unified series of apparatus and comparable methods for
determining thermal conductivity under a wide range of tem-
peratures.

The setup for conductivity measurements of refractories
up to 2673 K (2400°C) consists of four main systems:

1. the apparatus for determining conductivity;

2. the vacuum system;

3. the power supply;

4. the measurement system for power and temperature.

Apparatus for Thermal Conductivity Determination

Fig. 12 shows the apparatus placed inside a vacuum cham-
ber. The casing of the apparatus is a 595 x 490 x 250 mm
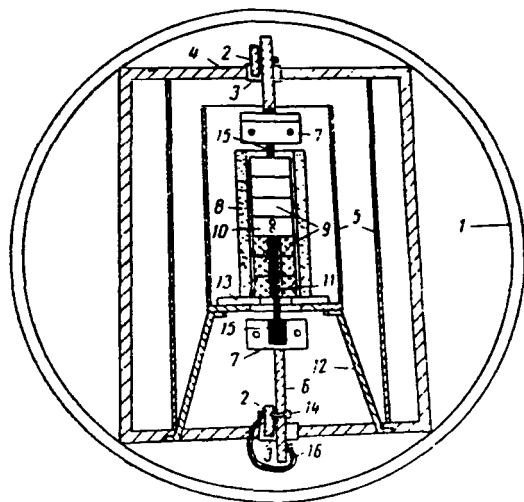parallelopiped of 25 mm angles, which can be taken out of the

Fig. 12.Apparatus for determining conductivity of highly refractory materials in vacuum, up to temperatures close to their melting point.

1 - vacuum chamber; 2 - copper bus-bar; 3 - asbestos-cement packing; 4 - casing; 5 - screen; 6 - copper electrode; 7 - graphite electrode; 8 - molybdenum box casing; 9 - guards; 10 - sample; 11 - heater; 12 - support; 13 - zirconium dioxide plate; 14 - bolt; 15 - wire for recording voltage drop; 16 - leads of laminated copper sheets.

chamber along with the whole apparatus after disconnecting the mains. A portable casing is convenient for mounting and repairs, because the electrodes and the screens could be connected outside the vacuum chamber. Steel supports 12 and asbestos cement packing 3 are fixed to the lower plate of the frame. The current-carrying bus bar 2 lies freely in the packing. Similar packing and bus bar are attached to the top plate. The first of the screens 5, made of 2 mm iron sheet, is attached to the frame.

The electrodes, which fix the heater, consist of copper bus bars 2, to which a graphite split contact 7 is screwed in with two steel bolts. The graphite plate is pressed on to the heavier graphite mass with two bolts, thereby keeping the heater 11 in position. The upper electrode is firmly attached to the copper bus bar with a bolt and the lower one hangs freely on the heater. Bolt 14 fixes the lower electrode only at the time of mounting the heater. The free hanging of the lower electrode compensates for the thermal expansion of the heater.

31

Electric current is led in through the large vacuum inlets to which the bus bars 2 are connected through leads of laminated copper sheets.

The radiation-shield system consists of a first layer of flat shields of 2 mm iron sheet fixed on the frame, a second layer of flat shields and a third layer of cylindrical ones, each made of 1 mm. sheet iron. The second layer of radiation shields is attached to the upper and lower plates of the frame and semicircular shields are attached to the front and back screens.

Graphite tubes and 5 mm tungsten wire serve as heating elements.

The graphite heater not only enabled the use of the same samples which were used for the wire heater method, but made it possible to obtain considerably higher temperatures [2373 to 2473 K (2100 to 2200°C)]. It is very strong, but at high temperatures, graphite vaporizes considerably, thereby dirtying the samples and reacts with some of the materials under investitation (for example with zirconium dioxide at 2200 to 2400°C) to form carbides.

A tungsten heater makes the samples less dirty,and reacts less with the test materials. But the electrical resistance of tungsten wire is about half that of graphite, which causes a number of technical difficulties in obtaining high temperatures.

While conducting the tests, both types of heaters were used, though, as a whole, the tungsten wire heating was more successful. It is also to be borne in mind that the cross section of the graphite heater is about 10 times that of tungsten wire and so the heat losses along the heater axis for tungsten would be less, even after accounting for the difference in thermal conductivities.

Owing to the small diameter of the tungsten heater, the outside and inside diameters of the test cylinder (Fig. 13) and, consequently, the heat losses through its ends could be reduced.

The influence of the cross section area on the accuracy of measurement was determined experimentally, by using graphite samples of different outside diameters. It appears from Fig. 14

32

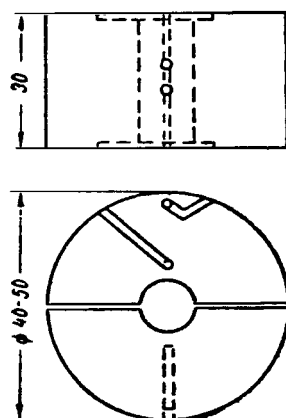**Fig. 13.** *Sample for measuring thermal conductivity up to the melting point of highly refractory materials (2000 to 2500°C).*

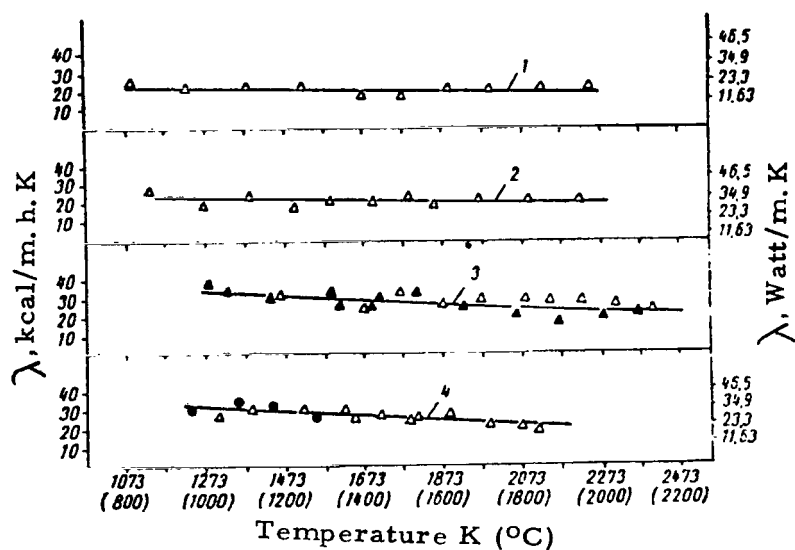**Fig. 14.** *Thermal conductivity of graphite electrodes during tests on cylinders of different diameters.*

	1	2	3	4
outside dia., mm	20	30	40	50
cross section area, mm^2	314	706.5	1256	1962.5

33

that, for a certain cross section (outside diameter less than 40 mm), good reproducibility was obtained in the entire temperature range; but for larger sections (outside diameter 40 to 50 mm), and particularly at temperatures 1773 K the thermal conductivity values were somewhat higher at higher heat inputs.

The test cylinder, consisting of six guards 9 (Fig. 12) and one sample 10 in the middle, is mounted after the heater is fixed in position.* The guards and the sample have the same heights, same outside and inside diameters. They should also have nearly the same conductivity.

The semicircular rings of the test cylinder are so set that the gaps between the semicircular rings lie crisscross (to reduce the radiation losses from the heater) and the temperature sensing holes in the sample and heater are situated along the vacuum chamber axis to facilitate temperature readings through an observation window in the chamber.

On the cold face side, the cylinder is surrounded by a split box 8 made of molybdenum strips with tungsten coverings at the surface of contact with the cylinder. The casing is filled with porous granules of zirconium dioxide*. Up to the highest temperature of investigations (2300 to 2400°C at the hot face of the sample, 2100 to 2200°C on the side facing the casing) such a casing did not fail even once during use and remained almost intact, without any deterioration during working**.

The vacuum system consists of a vacuum chamber of 0.5 m^3 volume, high vacuum diffusion pump of 1000 ℓ /sec capacity, fore-pump Type VN-1 and vacuum mains. Such a large vacuum system enables to exhaust up to 1 x 10^{-4} mm– HgCol in the whole temperature range and to maintain the high vacuum during all the measurements. Vacuum control is done continuously by vacuum-meters fitted with pressure control lamp (vacuostats).

---

*The technology of preparation and the filler material were developed by A.A. Pirogov [6], who provided us with the necessary quantities of the powder for vacuum experiments.

**Other possible screen-casings were also tried. Lightweight high-alumina refractory works satisfactorily up to 1500°C; at higher temperatures, thermal deterioration and gas occlusions are observed. Heat treated zirconium dioxide used for the casing has sufficient refractoriness but low endurance (i.e.. its insulation breaks down by prolonged heating).

The electrical power system comprises a primary trans-
former, Type AOSK 25/0.5 of 25 kw, capable of insuring smooth
change of voltage from 0 to 250 V at a working current of 110
amp, and a secondary power transformer, Type TPO-102 of
10 kw (maximum current 800 amp. at 12 V). The current was
measured with the help of current transformers of precision
class 0.2 (Type UTT-5 for up to 600 amp., UTT-6 above
600 amp.), and the potential drop was measured with the help
of voltmeters of precision class 0.5 having low power consump-
tion.

The temperature drop was measured with the help of
thermocouples. At high temperatures and in electrically conduct-
ing samples, it was measured with an optical pyrometer through
an observation window on the cover of the vacuum chamber. The
absorption loss through the 5 mm thick glass piece was deter-
mined, at the time of measuring the temperatures, in several
ways: with a standard pyrometer strip lamp, on a foil of 20%
RhPt in air, and on a graphite heater by superposing another
observation glass. The mean values of the corrections applied
for the absorption are given in Fig. 15.
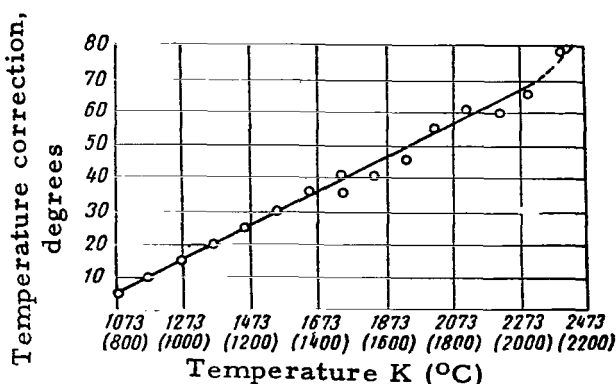
Fig. 15. *Absorption correction for the glass, for temperature measurements
with optical pyrometer.*

Thermal conductivity at 2673 and 2273 K was measured in
vacuum and in atmospheres of nitrogen and argon. The maxi-
mum temperature was reached by putting on power at not more
than 10 kw.

The mean square deviation of the results, which shows the
reproducibility of measurements, lies between 2.5 to 5% for
low conducting samples (1 to 3 kcal/m.h.K., i.e., 1.16 to

35

3.5 Watt/m. K) and 10 to 15% for highly conducting samples (10 to 20 kcal/m. h. K. , i. e. , 11.63 to 23.3 Watt/m. K).

The time required for an investigation on the temperature-thermal conductivity relationships, of a sample, from 1173 K (900°C) to the maximum temperature -- taking measurements at about 8 points, and including the time for loading and pumping out the air -- is 7 to 8 hours.

A comparison of the results obtained by using wire heaters up to 1973 K (1700°C) (Section 3) and those obtained by using the tungsten and graphite heaters shows that under a given set of conditions of the test cylinder and thermal conductivity, the values of thermal conductivity obtained with graphite and tungsten heaters are higher. Considerably higher (above 40%) values were found in the case of low conductivity materials (of the order of 1 kcal/m. h. K), amounting to an increase of about 15% for materials having thermal conductivity 4 to 5 kcal/m. h. K (4.65 to 5.81 Watt/m. K). For higher conductivity materials (graphite, zirconium diboride, etc.), the difference was within experimental errors.

The abovementioned increase in conductivity values for low conductivity materials is reduced as the temperature increases and as graphite heaters are substituted by tungsten heaters. The latter have a lesser cross section of test cylinder than the graphite ones.

The difference in the conductivity values obtained on different apparatus could be explained on the basis of different amounts of heat disspation at the heater surface. For wire heaters, the heat losses through the 0.9 mm diameter wire along the uncooled surface and along the former of the heater are very small compared to the heat dissipation of rod-heaters through the large water-cooled graphite and copper electrodes.

When the thermal conductivity of a sample is approximately equal to that of the heater (graphited materials, carbides, borides, nitrides), the heat flow is radial. The heat flow along the length of the heater being negligible (due to the difference in the path length for heat flow), there is good agreement in the results for highly conducting materials. The cross section of the heater should be reduced and its length increased, in order to minimize the heat transfer along the heater axis.

Therefore, the method described above, specially developed for high temperature-cum-vacuum measurements with large tungsten and graphite heaters, should be used only for studying the thermal properties of materials whose conductivity is more than 10 kcal/m. h. K. For materials with lesser thermal conductivity, the errors in this method are quite large.

Let us now estimate the maximum theoretical error of measurements at high temperature under vacuum.

As shown earlier (2),

$$\frac{\Delta \lambda}{\lambda} = \left[\frac{\Delta I}{I} + \frac{\Delta V}{V} + \frac{\Delta T_1 + \Delta T_2}{T_2 - T_1} + \frac{1}{\ln \frac{\lambda_1}{\lambda_2}} \left(\frac{\Delta \lambda_1}{\lambda_1} + \frac{\Delta \lambda_2}{\lambda_2} \right) + \frac{\Delta \ell}{\ell} \right] 100\%.$$

The degree of accuracy of the instruments used (the voltmeter and the ammeter with its current transformer, etc.) was such that:

$$\frac{\Delta I}{I} = 0.5\% ; \quad \frac{\Delta V}{V} = 0.5\% ;$$

$\Delta \lambda_1 = \Delta \lambda_2 = 0.5$ mm; $\Delta \ell$ is the accuracy of length measurements.

For the selected sample dimensions and accounting for deviations from the nominal positions of individual holes:

$$\lambda_2 = 5.5 \text{ to } 8.1 \text{ mm};$$

$$\lambda_1 = 17.2 \text{ to } 24.1 \text{ mm};$$

$$\ln \frac{\lambda_1}{\lambda_1} = 0.83 \text{ to } 1.19.$$

Substituting all these values, the errors in length measurements come to 10.3%. This relatively high error is due to the small dimensions of the sample.

The errors in temperature measurements depend on the thermal conductivity of test materials and on the temperature concerned (Tables 6 and 7).

TABLE 6

Relationship between the temperature drop ($T_2 - T_1$) and thermal conductivity of the material at various test temperatures

Material	Thermal cond. kcal/m.h.K (Watt/m.K)	Temperature drop ($T_2 - T_1$)											
		900 (1173)	1000 (1273)	1100 (1373)	1200 (1473)	1300 (1573)	1400 (1673)	1500 (1773)	1600 (1873)	1700 (1973)	1800 (2073)	1900 (2173)	2000 (2273)
Zirconium di-oxide, zirco-nates	1-2 (1.16-2.3)	140	-	195	220	-	260	~	315	370	-	-	475
Spinel, oxide of aluminum	4-5 (4.15-5.82)	-	75	90	115	145	185	220	250	285	-	340	-
Carbides, nitrides, silicides	10-20 (11.63-23.3)	45	-	75	100	-	140	-	-	-	-	-	-
Graphites, carbides, borides, nitrides	22 (25.6)	15	-	25	30	40	55	60	-	75	90	-	145

TABLE 7

Dependence of percentage errors in temperature measurements using an optical pyrometer of an accuracy of ±5 K, at different test temperatures of various types of materials

Material	Thermal cond. kcal/m.h.K (Watt/m.K)	Percentage error $\dfrac{\Delta T.100}{T_2 - T_1}$, % at test temperature; °C (K)											
		900 (1173)	1000 (1273)	1100 (1373)	1200 (1473)	1300 (1573)	1400 (1673)	1500 (1773)	1600 (1873)	1700 (1973)	1800 (2073)	1900 (2173)	2000 (2273)
Zirconium dioxide, zirconates	1-2 (1.16-2.3)	3.7	-	2.56	2.27	-	1.92	-	1.85	1.35	-	-	1.05
Spinel, oxide of aluminum	4-5 (4.15-5.82)	-	6.7	5.6	4.35	3.45	2.70	2.25	2.00	1.75	-	1.45	-
Nitrides, carbides, silicides	10-20 (11.63-23.3)	11.1	-	6.65	5.0	-	3.55						
Graphites, carbides, borides, nitrides	>20 (>23.3)	33.0	-	20.0	16.5	12.5	9.1	8.3	-	6.7	5.45	-	3.45

The maximum theoretical error in this high temperature method for thermal conductivity measurement depends on:

a) error in length determinations ($\pm 10.3\%$);

b) error in power determination ($\pm 1\%$);

c) error in temperature measurements (which depends on conductivity of the material and on temperature). The errors are as follows: for material with high thermal conductivity [50 kcal/m. h. K (58.1 Watt/m. K) at 1173 K (900°C)] 66%; for material with thermal conductivity around 2 kcal/m. h. K (2.33 Watt/m. K) at the highest temperatures, 2%.

The mean square deviation of the results: for samples with thermal conductivity 2 kcal/m. h. K (2.33 Watt/m. K), 2 to 5%; for samples with conductivity 10 to 20 kcal/m. h. K (11.63 to 23.3 Watt/m. K), 10 to 15%; for samples with thermal conductivity 50 kcal/m. h. K (58.1 Watt/m. K), 12%.

CHAPTER II

LAWS GOVERNING THERMAL CONDUCTIVITY VARIATIONS IN REFRACTORY MATERIALS

1. General Characteristic of Refractories from the Heat Exchange Point of View

Refractories, i.e., materials with high melting points, are widely used in science and technology. Thus, refractory metals of high melting points (tungsten, tantalum, molybdenum, niobium), substances with conductivity similar to metals (carbides, nitrides, graphite, carbon dioxide), semiconductors (chromium oxide, zirconium dioxide) and insulators (insulating oxides, zirconates) -- all these could be classified as refractory materials.

Multicomponent systems (solid solutions, and multiphase systems), as well as single-phase, single-component systems are used. A refractory can have crystalline (crystalline quartz) or amorphous structure (quartz glass).

The following oxides form the main components of refractories both in pure form and in compounds and solid solutions:

BeO, MgO, CaO, ZnO, NiO, FeO, BaO, MnO, CoO, SrO, UO_2, TiO_2, ThO_2, ZrO_2, SiO_2, HfO_2, Ce_2O_3, SnO_2, Cr_2O_3, Fe_2O_3, La_2O_3, Ga_2O_3, Y_2O_3, V_2O_3, Ta_2O_5, Al_2O_3.

$MgO.Al_2O_3$ (mineral spinel); $ZrO_2.SiO_2$ (zircon); $3Al_2O_3.2SiO_2$ (mullite); $2MgO.SiO_2$ (forsterite) are the more common chemical compounds in use.

The heat transfer in a hard crystalline substance is brought about by elastic oscillations of the lattice (lattice thermal conductivity) and conductance electrons (electronic thermal conductivity) and in the case of porous semiconductors by the diffusion of pores.

A. F. Ioffe [7] showed that in the case of metals and semi-conductors, the electronic and lattice parts of the thermal conductivity of the solid are additive, i. e.,

$$\lambda = \lambda_{lattice} + \lambda_{electronic} . \tag{6}$$

The proportion of each of the components in the total conductivity is different, depending on the electronic structure of the solid material. In metals, the concentration of conduct-ance electrons is of the order of $10^{22}/cm^3$. Hence for chromium-nickel steels with low percentage of additives [8] the electronic conductivity part is 77 to 89% of the total conductivity. In addi-tion, the conductance electrons facilitate dispersion of elastic waves in electrons, i. e., they also influence the lattice conducti-vity indirectly.

Roughly speaking, the influence of electrons on thermal conductivity is about twice that of the elastic oscillations of the lattice.

It has been shown by V. E. Ivanov and V. V. Lebedyev [9] that for W, Mo, Cu, Au at room temperature, $\lambda_{lattice}$ (phononic) constitutes 10 to 20% of $\lambda_{measured}$, and at 673 to 773 K (400 to 500°C) $\lambda_{lattice}$ is considerably smaller in percentage.

The electron concentration in semiconductors is $10^{14}/cm^3$, i. e., $\lambda_{measured}$ approximately equals $\lambda_{lattice}$. For example, electronic thermal conductivity of zirconium dioxide, a refractory semiconductor of small resistance, reaches only 0.2% of the total conductivity at considerably high temperatures (2073 K, i. e., 1800°C).

Refractory oxides are either insulators or semiconductors. The more common refractory oxides are mainly insulators: MgO, BeO, Al_2O_3, SiO_2, ThO_2. Consequently, the laws govern-ing variations in thermal conductivity in such materials are determined by the conductivity of the lattice.

Experimental results of investigations on the laws of thermal conductivity of refractory insulators and of the various crystalline modifications, which are commonly met with in refractory practice and in the investigations of temperature relationships of the conductivity of insulators above the charac-teristic temperature (right up to the melting point of selected materials), are given in this chapter.

2. Relation Between Thermal Conductivity of Refractory Insulators and Temperature

The samples were made of pure materials during these temperature-thermal conductivity studies. They had low porosity, in order to practically eliminate the effect of pores.

Measurements were conducted in a wide temperature range extending up to the pre-melting region.

Investigations on polycrystalline Al_2O_3, prepared by pressing from fine powder (less than 2 microns), with an open porosity of 0.02 to 0.56% and a mass-density 3.76 to 3.80 g/cm^3, showed that thermal conductivity is reduced in the temperature range 773 to 1073 K (500 to 800 °C) and that with further increase in temperature, it remains constant within $\pm$ 10% (4.5 kcal/m.h.K) up to the highest temperature experimented with (1993 K). It appears from the $(\frac{1}{\lambda})$ vs. T relationship (Fig. 16) that in the temperature range 773 to 1073 K (500 to 800°C) the variation of ($\frac{1}{\lambda}$) $\sim$ T is quite regular*.

Since the character of the λ (T) function has a basic importance, avoidable inaccuracies in high temperature investigations were eliminated by measuring the temperature drop by suitable methods, e.g. by thermocouple and electric pyrometer (on cold face) and thermocouples (on hot face). It should be emphasized that no increase in thermal conductivity was noticed after reaching a minimum value. However, some differences were observed on comparison with the values obtained by the hollow ellipsoid method [11]. The minimum values of absolute λ for Al_2O_3 [19] are close to one another (in Fig. 16), though they are attained at high temperatures (1473 to 1673 K). The main difference is that McQuarrie [10] noticed an increase in the thermal conductivity at 1673 K, but in the experiments described here, the conductivity remained constant almost up to the melting point. The accuracy of measurements being greater now than in [11], it can be surmised that the increase in thermal conductivity of Al_2O_3 noticed in [10] was caused by some appreciable experimental errors, and by the arbitrariness adopted in passing the curve through the experimental points. It should be

---

*The deviation in the thermal conductivity values from those of published data [3] could, according to us, be attributed to the difference in the purity of sample.

noted that other authors [12] also did not record an increase in thermal conductivity at pre-melt temperatures.
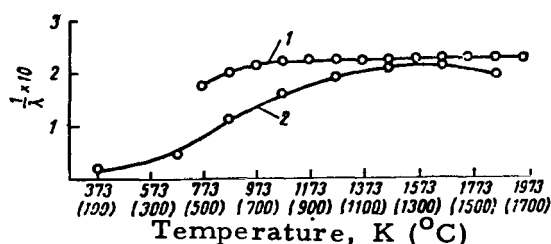

Fig. 16. *Variation of thermal resistance of polycrystalline Al$_2$O$_3$ with temperature.*

1 - author's data; 2 - data of Kingery et al [3].

Thermal conductivity measurements of polycrystalline magnesium oxide of zero porosity revealed two regions (Fig. 17) with different relationships between temperature and conductivity: the range 1173 to 1573 K (900 to 1300°C), in which the

$\lambda \sim \dfrac{1}{T}$ relationship holds good, and the range 1473 to 2023 K

(1200 to 1750°C) in which thermal conductivity remains constant within 4% (which is better than the accuracy of the method). For further verification of the nature of variation with temperature, experiments were conducted at still higher temperatures. Measurements in an argon atmosphere did not reveal an increase in the conductivity up to 2223 K (1950°C), the temperature at the internal surface of the sample being about 2323 K. Similar results were obtained for MgO with 2.5% forsterite.
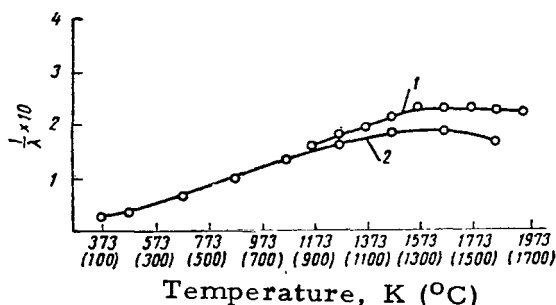

Fig. 17. *Variation of thermal resistance of polycrystalline MGO with temperature.*

1 - data of the present investigation; data of Kingery et al [3].

44

An increase in thermal conductivity was also noted in [10] for BeO at temperatures above 1473 K. Though the present investigations did not include BeO, it is appropriate to note that recent measurements on BeO and on a mixture of BeO with 1% Al up to 2373 K [13] showed an increase in thermal conductivity, only at temperatures higher than 2073 K.

It should also be pointed out that high temperature measurements for uranium dioxide [14] did not show a minimum value of thermal conductivity up to 2373 K.

Thus, there is a group of substances (Al_2O_3, MgO, UO_2) in refractory insulators, which have the following peculiarities: there exists a very high maximum value of conductivity in the lower temperature region; the $\lambda \sim \frac{1}{T}$ relationship holds good from the Debye temperature up to 1273 K (Al_2O_3, MgO), 2173 K (BeO), 2373 K (UO_2); a minimum value of λ is obtained at high temperatures, due to the mean free path of phonons becoming comparable to the interatomic distances in the crystal lattice.

The increase in thermal conductivity after reaching a minimum, which was interpreted as a definite law by some authors [15, 10, 16, 17] appears controversial, as also all the explanations given for this phenomenon. The materials discussed herein are characterized by quite high Debye temperatures (800 to 1000 K).

Measurements on quartz (Fig. 18) in the temperature range up to 1773 K on the hot face (average temperature 1400 K) show that another variety of substances exists among refractory insulators, for which thermal conductivity has an increasing character throughout the temperature range of 273 K (0 °C) to temperatures close to their melting point. However, for crystalline quartz, thermal conductivity increases only after it has attained a minimum possible value, which corresponds to the mean free path of phonons, and is comparable with the interatomic distances.

The temperature-conductivity relationship for quartz, in a wide range of temperatures (from 4 K to the melting point), has the following peculiarities: a low maximum for thermal conductivity (λ_{max} for quartz is about one-sixth of that for Al_2O_3); the range of minimum values of conductivity lies around 473 K; the thermal conductivity increases from 373 K (Fig. 18) up to the
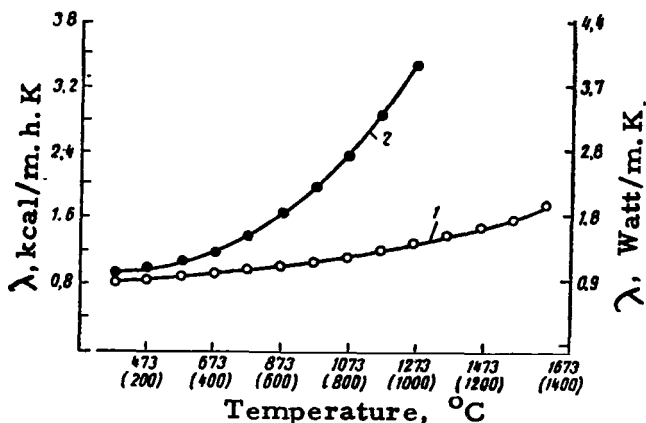
Fig. 18. Temperature-- thermal conductivity characteristic of polycrystalline quartz (1) and quartz glass (2).

melting point; for quartz, λ_{max} occurs at 10 K (compared to 50 K for Al_2O_3 and 110 K for MgO), and the Debye temperature is around 250 K (compared to 700 K for MgO and 750 K for Al_2O_3).

At temperatures above 273 K ($0^{o}C$), a similar pattern is observed for polycrystalline zirconium dioxide (Fig. 19) and for calcium, barium and strontium zirconates (Fig. 20) in the thermal conductivity —temperature relationship.
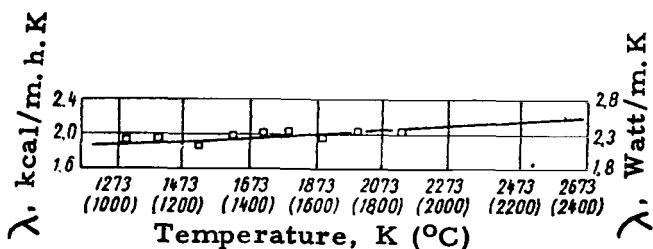

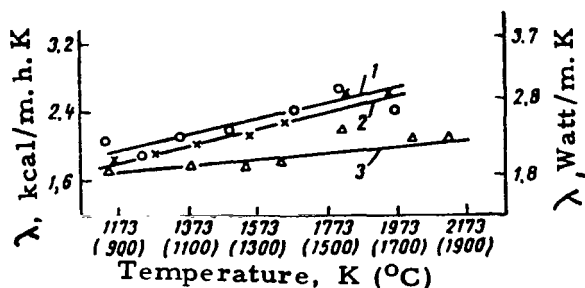**Fig. 19. Temperature -- thermal conductivity relationship for polycrystalline zirconium dioxide.**

46

Fig. 20. Temperature -- thermal conductivity relationship for zirconates.
1 - strontium zirconate (SrZrO_3); 2 - calcium zirconate (CaZrO_3);
3 - barium zirconate (BaZrO_3).

3. Thermal Conductivity of Refractories Formed by Combinations of Al_2O_3 and SiO_2

Al_2O_3-based refractories are widely used in industry. The Al_2O_3 content varies widely -- from 100% (corundum) to 30 to 35% (fire-brick). Silica SiO_2 is the second major constituent.

Thermal conductivity of several materials with different Al_2O_3 and SiO_2 contents was determined in order to study the laws of variation of thermal conductivity in the Al_2O_3-SiO_2 system.

Figs. 21 and 22 show the experimental curves of the thermal conductivity -- temperature relationship, for dense and porous materials. Some properties of the investigated materials are given in Table 8, while experimental values of thermal conductivity are shown in Tables 9 and 10.

Thermal conductivity variation curves, depending on the Al_2O_3 content, are shown in Fig. 23 (for dense materials[1]) and Fig. 24 (for porous materials).

In the binary system Al_2O_3-SiO_2, the laws of variation of thermal conductivity are applicable to only dense alumina-silicate materials, after applying corrections for the presence of additives and for non-zero porosity (see Figs. 21, 23). In the porous ceramics of the Al_2O_3- SiO_2 system, the laws obtained are distorted due to porosity and are considerably dependent on the distribution of pores according to size.

---

[1] Here dense material means a material with porosity up to 20 to 25%, for which simple computation to zero porosity is valid.

47

TABLE 8

Some properties of alumina-silicate materials

Refractory type	Chemical composition, %					Mineralogical composition	Packing density g/cm^3	Apparent porosity %	Water permeability ml/min*
	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	CaO	MgO				
Corundum	97	1.00	0.18	0.10	0.44	Sample consists essentially of corundum	2.96	24.0	8.4
High alumina-content	83.19	13.6	0.46	0.6	0.58	Corundum 80%, vitreous substance 15 to 18%	3.06	9.4	9.2
	82.84	13.7	0.56	0.61	0.50	-	Not determined	10.0	1.72
	77.6							17.0	-
	72.98	23.22	0.84	0.75	0.72	Corundum, mullite 80%, vitreous substance 20%	2.55	16.5	3.71
	68.3	25.1	0.70	0.75	1.80	Mullite, corundum 73%	2.51	16.5	3.5
Kaolin (from Novoselitsk)	42.9	52.7	0.92	0.60	0.57	Mullite, corundum 53%, vitreous substance 47%	2.38	12.4	1.66
Blast furnace firebrick	35.9	58.3	1.26	0.59	0.72	Mullite, corundum 37%, vitreous substance 63%	2.10	15.1	4.5
High alumina, lightweight	81.0	16.54	0.36	0.46	0.50	-	1.40	55.8	64.12

*Water permeability means the rate of penetration of water under a certain pressure through a certain thickness of the sample.

TABLE 9

Thermal conductivity of dense refractories of the Al_2O_3 - SiO_2 system for various temperatures (Calculated for zero porosity by the formula: $\lambda_p = \lambda_o (1 - p)$

Refractory type	Chemical composition %		Porosity %	Thermal conductivity, kcal/m.h.K at test temperature °C (K)					
	Al_2O_3	SiO_2		200 (473)	400 (673)	600 (873)	800 (1073)	1000 (1273)	1200 (1473)
Corundum	97.0	1.00	24.0	5.80	3.89	3.50	3.16	3.16	3.16
High alumina content	83.19	13.6	9.4	2.05	1.61	1.53	1.61	1.72	1.81
	82.84	13.7	10.0	3.11	2.18	1.94	1.94	-	-
	72.98	23.22	16.5	3.37	2.97	2.80	2.75	2.69	2.66
	68.3	25.1	16.5	1.34	1.53	1.75	1.92	1.97	2.04
Kaolin (from Novo-selitsk)	42.9	52.7	12.4	1.46	1.64	1.83	1.97	2.01	2.06
Firebrick (blast furnace)	35.9	28.3	15.1	0.80	0.90	0.97	1.06	1.18	1.27
Al_2O_3 [3]	100	-	4.5-7.3	18.3	10.8	7.48	5.90	5.05	4.53
Natural quartzite (crushed)	1.90	97.6	{ Close {to zero	0.86	0.94	1.02	1.14	1.30	1.50

TABLE 10

Thermal conductivity of porous (lightweight) refractories of the Al_2O_3 - SiO_2 system

| Refractory type	Real porosity %	Chemical composition %		Thermal conductivity, kcal/m.h.K, at temperature K (°C)						Microstructure (Petrographic analysis)
		Al_2O_3	SiO_2	473 (200)	673 (400)	873 (600)	1073 (800)	1273 (1000)	1473 (1200)	
Corundum, lightweight	80	95.4	3.08	2.03	1.50	1.25	1.13	1.07	1.04	Pores round, closed; dominant size 0.3 to 0.9 mm, max 3 mm
Corundum lightweight	82.5	95.9	3.40	1.32	1.02	0.92	0.91	0.95	1.01	Pores round, closed; dominant size 0.6 to 1.4 mm, max 1.6 mm
High alumina, lightweight	55.8 `70	81.0 44.14	16.54 51.96	0.74 0.55	0.64 0.56	0.64 0.60	0.66 0.72	0.68 0.83	0.70 0.95	Pores round, closed; dominant size up to 1.2 mm
Firebrick, lightweight	59.3	31.2	62.7	0.29	0.33	0.37	0.41	0.45	-	Pores of irregular shape, 0.3 to 0.9 mm, open, max. size 1.5 mm
Firebrick, ultralight	88	35.73	57.9	0.17	0.21	0.24	0.28	0.30	-	Pores round, closed, dominant size 0.1 to 0.2 mm, max. 0.4 mm
Dinas lightweight	53.5	1.75	92.95	0.58	0.65	0.73	0.80	0.88	0.95	Pores of irregular shape, closed; dominant size 0.3 to 1.2 mm; max 2.5 mm
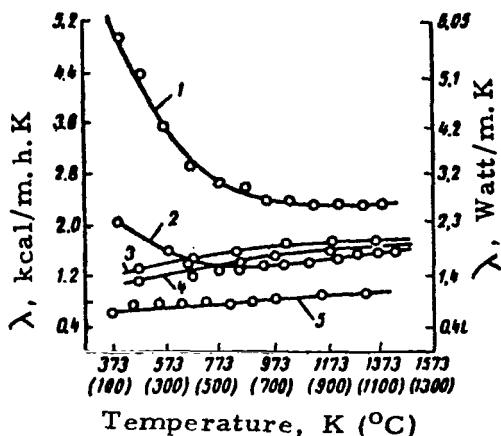
Fig. 21. Temperature-thermal conductivity relationship of refractories of the Al_2O_3 — SiO_2 system (materials with a porosity at which computation to zero porosity is valid).

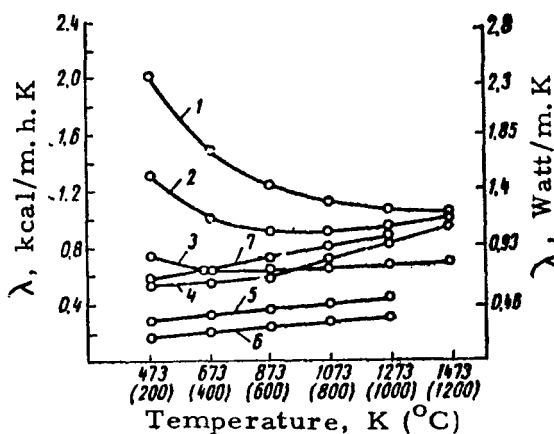|	1	2	3	4	5
Al_2O_3 content, %	97.0	82.2	63.3	45.0	37.35
Apparent porosity, %	24	12.7-13.5	16.5	12.4	15.1

Fig. 22. Temperature — effective thermal conductivity relationship of the Al_2O_3 - SiO_2 refractories (porous materials).

	1	2	3	4	5	6	7
Al_2O_3 content, %	95.4	95.9	81.0	44.4	31.2	35.73	1.75
porosity, %	80	82.5	55.8	70	59.3	88	57.3*

---

*Lightweight Dinas

51

Since all parameters could not be insured to be identical due to technological difficulties, the thermal conductivity data for the samples of alumina-silicate materials (Fig. 22 to 24) are only particular cases from the point of view of the study of the binary system. ·
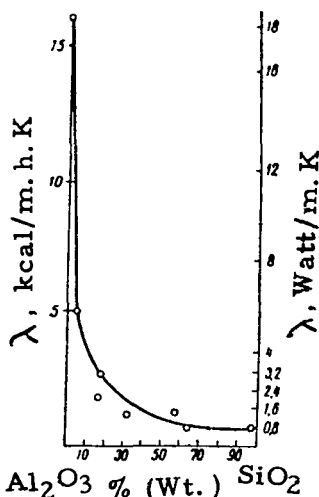

Fig. 23.Curve showing variation of thermal conductivity with concentration of consti- tuents of refractories of the Al_2O_3 - SiO_2 system (dense materials) at $200^{\circ}C$ (473 K).
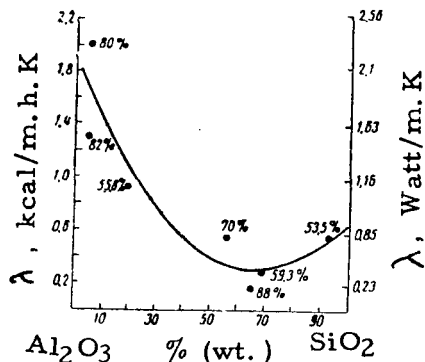
Fig. 24.Relationship of thermal conductivity with con- centration of constituents of refractories of the Al_2O_3 - SiO_2 system (highly porous) (the numbers on the curve indicate porosity).

A reduction in thermal conductivity with an increase in the SiO_2 content is observed in dense alumina-silicate materials (Fig. 23). The reduction is especially sharp under relatively very low silica concentrations (5% by weight SiO_2). With further increase in silica content, thermal conductivity of the system decreases continuously throughout the concentration range.

Marked difference (of more than one order of magnitude) in thermal conductivities of the pure components is charac- teristic of the Al_2O_3 - SiO_2 system. At 373 to 473 K, the low conducting components have the minimum possible thermal con- ductivity values, which correspond to mean free path of phonons and are comparable in magnitude to interatomic spaces. This peculiarity results in an unsymmetrical concentration curve, which is different from the usual U-curve observed for compo- nents of equal thermal conductivity [18, 19]. For highly porous

materials (Fig. 24) also, the unsymmetrical concentration curve is possible, but appreciable difference in porosity is noticed and calculation at zero porosity is not reliable.

A sharp change in the temperature characteristic is also noticed in the Al_2O_3 system. While studying the causes for such a change, it is necessary to consider the mineralogical changes that take place in the system with various Al_2O_3 and SiO_2 contents.

Table 8 gives the results of petrographic studies on samples. With a decrease in Al_2O_3 content and simultaneous increase of silica, the corundum content of the sample is reduced because of mullite formation ($3Al_2O_3 \cdot 2SiO_2$). A part of the silica forms a vitreous substance.

For example, with 83.19% Al_2O_3 (13.6% SiO_2), a microscopic examination of the sample revealed 15 to 18% vitreous substance and 1 to 2% mullite. In the concentration range 70 to 85% Al_2O_3, a large quantity of mullite (65%) was formed, while the vitreous substance remained constant. With further increase in SiO_2 content, two phases were revealed in the sample, viz., mullite and vitreous substance.

Similar phase changes were observed by V. A. Kopeĭkin and D. N. Poluboyarinov [20]. Chemical analysis showed that the quantity of the vitreous substance phase increased at $<$ 77% Al_2O_3. X-ray investigations showed that for pure materials, the vitreous substance phase appears earlier ($<$ 85% Al_2O_3) than for industrial materials ($<$ 75% Al_2O_3).

Thus there can, in general, be three phases in the Al_2O_3— SiO_2 system samples, namely, mullite, corundum and vitreous substance.

From the diagram, it will be seen that one of the phases exists in negligible quantities and so in practice there are only two phases: corundum — glass or, mullite — glass. The mineralogical composition determines the change in the character of the temperature relationship. For Al_2O_3 and mullite,

$\lambda \sim \dfrac{1}{T}$; for the vitreous substance, $\lambda \sim T^3$. The thermal conductivity of Al_2O_3 is about 1.5 times that of mullite.

In general

$$\lambda = c_1 \cdot \frac{a}{T} + c_2 \cdot \frac{b}{T} + c_3 \cdot dT^3 \tag{7}$$

where c_1, c_2, c_3 are concentrations of corundum, mullite, and glass respectively.

and a, b, d are constants, a $>$ b

Since with changes in Al_2O_3 and SiO_2 concentrations the phase composition changes in the sequence: corundum $\rightarrow$ glass $\rightarrow$ mullite, the values of the terms in (7) also change. Hence with an increase in silica content the temperature—conductivity relationship changes from $\lambda \sim \frac{1}{T}$ to $\lambda \sim$ T.

4. Thermal Conductivity of the System: Crystalline Silica—Quartz Glass

Quartz glass refractory is quite commonly used in industry. It is well known that at a certain temperature quartz crystallizes into crystobalite [21 to 24]. The temperature and time required for complete crystallization at a given temperature depend on the mass of the sample, time for temperature rise, etc.

The crystalline phase sets in, in the glass-cracks and around the pores, in the form of metastable crystobalite. Later on, this transforms into stable crystobalite and spreads in all directions from the origin of the cyrstalline phase.

Closed pores open out during crystallization, and at 1673 K all the pores become open. Along with this, the porosity is increased to some extent. The incremental change in porosity is of course small, of the order of a few percent. Thus, the structure of quartz glass rapidly changes during sustained heating (this also happens in equipments in which quartz glass is used as refractory). Accordingly, it is possible to observe the change in the physical properties during the transition from amorphous to crystalline state as well as in the proportion of the amorphous and the crystalline phase in the specimen. Given one specimen of quartz glass, a series of different concentrations of the crystalline silica, i.e. quartz glass, can be obtained by sequential heat treatment.

Thermal conductivity of the two-phase system crystalline silica-quartz glass was studied by the author. A cylinder (height 90 mm, outside diameter 75 mm, inside diameter 20 mm) was cut out from a quartz glass block and this served as the sample for the experiments.

Sustained heating of the sample was done in a cryptol furnace — initially at 1673 K, and later on at 1773 and 1873 K to accelerate the crystallization process. After each heating, a small test piece of the sample was subjected to petrographic and X-ray analysis.

The quantity of crystobalite and variations in the microstructure during crystallization were checked by petrography (Table 11) and by the line intensity (111) of crystobalite on ionization curves. Fig.25 shows the growth of crystobalite formation with time of heating and temperature.
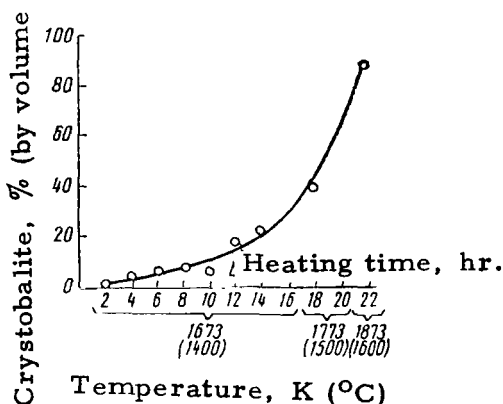

Fig. 25. Relationship between the quantity of crystallized quartz glass in crystobalite, time of heating, and temperature.

The variation of thermal conductivity with temperature was determined on the same sample, at intervals of 200 K. The relationship between the mean conductivity of quartz glass and crystobalite content is shown in Table 12 and in Fig. 26.

Thermal conductivity of original quartz glass (Fig. 27) increases negligibly with rise in temperature up to 623 or 673 K (350 or 400°C), in a manner similar to that of variations in the

55

TABLE 11

Variations in the microstructure of quartz glass during crystallization by heating

Temperature of heat, °C (K)	Holding time, h.	Pore size*, mm max.	Pore size*, mm dominant	Pore shape	Quartz %	Anisotropic, foliated β-crystobalite, %	Microstructure characteristics
Original quartz glass		0.35	0.02	Round			Silicates in the glass with weak crystallization, in the form of small additions
	2	0.32	0.04-0.12	Round and oval	2-3	1-2	Cracks with orientation
1400 (1673)	4	0.24	0.05-0.12	-do-	2	3-5	-do-
	6	0.32	0.08-0.20	Round, oval and irregular	1	5-7	Crystobalite in the form of radial rays. Many pores and thin cracks
	8	0.80	0.08-0.28	Elongated, rarely round	1	5-8	Cracks with orientation. Elongated-oval pores set in one direction
1400 (1673)	10	0.72	0.08-0.20	Round	traces	5-7	Cracks in different directions.
	12	0.20	0.04-0.13			16-18	
	14	0.40	0.05-0.16		—	20-23 (27%**).	Cracks with orientation and sections
1400 (1673)	16						-do-
1500 (1773)	2	0.30	0.08-0.15	-		55	
1400 (1673)	16						
1500 (1773)	4	0.60	0.10-0.20	Round and oval	-	85-90 (97%**)	Without any definite orientation
1600 (1873)	2						

* Pores in small numbers
**Data from X-ray analysis

TABLE 12

Thermal conductivity of the system SiO_2(crystobalite) - quartz glass, determined on quartz glass specimens with different crystobalite content

| Temperature of the heat, K (°C)	Holding time, h	Crystobalite content %	Thermal conductivity kcal/m.h.K at mean temperature K (°C)								
			473 (200)	573 (300)	673 (400)	773 (500)	873 (600)	973 (700)	1073 (800)	1173 (900)	1173 (1000)
	-	-	1.0	1.08	1.18	1.38	1.68	2.0	2.38	2.88	3.5
	2	1-2	0.88	0.96	1.07	1.2	1.36	1.66	2.00	2.44	2.90
	4	3-5	0.87	0.96	1.05	1.14	1.28	1.40	1.67	2.08	2.65
1673	6	5-7	0.68	0.78	0.9	1.08	1.26	1.48	1.08	2.2	2.58
(1400)	8	5-8	0.84	0.92	1.04	1.16	1.32	1.54	1.78	2.10	2.60
	10	5-7	0.84	0.92	1.04	1.16	1.32	1.54	1.78	2.10	2.0
	12	16-18	0.82	0.88	0.96	1.10	1.22	1.34	1.52	1.77	2.0
	16	20-23	0.66	0.8	0.92	1.08	1.26	1.48	1.68	1.92	2.16
1673 (1400)	16	55-60	1.02	1.10	1.18	1.28	1.42	1.62	1.82	2.08	2.34
1773 (1500)	2										
1673 (1400)	16										
1773 (1500)	4	85-90	0.86	0.9	0.94	0.98	1.02	1.06	1.14	1.22	1.30
1873 (1600)	2										
-	-	100	0.86	0.9	0.94	0.98	1.02	1.06	1.14	1.22	1.30

Crystobalite content, %
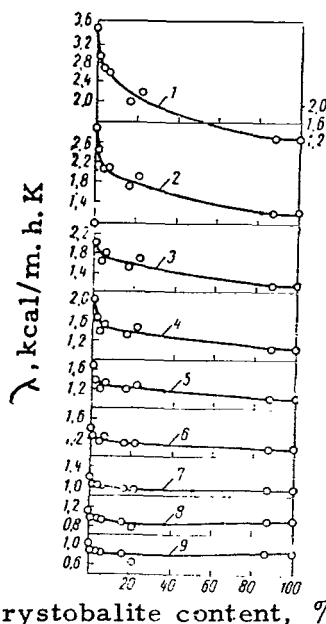
Fig. 26. Variation of thermal conductivity with concentration in the two-phase system quartz glass — crystalline silica (crystobalite), at temperatures.
1 - 1000°C (1275 K); 2 - 900°C (1173 K); 3 - 800°C (1073 K); 4 - 700°C (973 K); 5 - 600°C (873 K); 6 - 500°C (773 K); 7 400°C (673 K); 8 - 300°C (573 K); 9 - 200°C (473 K).

conductivity of high SiO_2 content materials. (See Section 5, Chapter III). With further increase in temperature, the thermal conductivity increases rapidly, because the heat flow by radiation increases due to high transparency of the material. This increase in conductivity is so large that at temperatures around 973 to 1023 K (700 to 800°C) the radiation component of conductivity becomes most predominant (Fig. 27).

The variation of thermal conductivity of quartz glass during crystallization in different temperature regions is different. It also varies with the concentrations.

The temperature range of measurements can provisionally be divided into two parts: 473 to 673 K (200 to 400°C) and 773 to 1273 K (500 to 1000°C) (See Fig. 26). In the first region, both
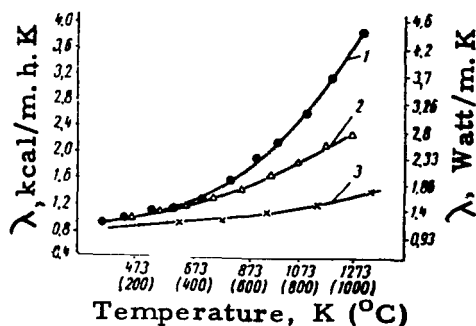
Fig. 27. *Variation of thermal conductivity of quartz glass with temperature and the extent of crystallization.*

1 - amorphous glass; 2 - glass with 40% crystobalite; 3 - reformed glass with 100% crystobalite.

the components have almost the same thermal conductivity and the transition of the concentration curve from the value for quartz glass to that of crystobalite is smooth and possesses a minimum which is difficult to distinguish. The more rapid decrease in thermal conductivity of quartz glass in the low concentration region can apparently be explained by the fact that at these temperatures, a part of the heat is carried by phonons. Therefore, even small quantities of the crystalline phase, with the cracks appearing therein, reduce transparency of tne material, leading to a rapid decrease in the mean free path of phonons.

In the temperature range 773 to 1273 K (500 to 1000°C), the two components in quartz glass have quite different thermal conductivities (one is twice that of the other at 1273 K) due to the increased heat transfer at these temperatures. The variation of thermal conductivity with concentration is more noticeable at small concentrations and the temperature rises considerably in the low concentration region (from 5 to 20%, by volume).

Thermal conductivity of the almost crystallized sample (Fig. 27), containing 85 to 90% crystobalite as shown by microscopic investigations and 97% as shown by X-ray analysis, varies with temperature in exactly the same way as in crystalline quartz (See Fig. 18). In this material, thermal conductivity has the same values as that of quartz (see Section 5). The experimental results show that the relationship between thermal conductivity of crystalline and amorphous SiO_2 depends on temperature.

59

The thermal conductivity of quartz at low temperatures in the region of maximum phonon conductivity is four times the thermal conductivity of quartz glass (Berman's experiments [25]). The disorder caused by neutron emission brings about a gradual decrease in the mean free path of phonons and a corresponding decrease in thermal conductivity. On the other hand, the thermal conductivity of amorphous quartz in the region of λ_{min} (i. e. about 273 K) is equal to that of crystalline quartz within experimental errors, and with increase in temperature, the latter considerably exceeds the former due to radiation.

Stabilization of the structure with the formation of a later order (crystallization of quartz glass) leads to a decrease in transparency and rapidly reduces the value of radiational thermal conductivity.

5. Thermal Conductivity of Refractories with High Silica Content

Refractory materials with high silica content (Dinas), form a widely used class of industrial refractories. They serve as a lining material for coke oven batteries, blast furnaces, glass furnaces and other equipment. High silica content materials consist of 85 to 90% SiO_2. Refractories of this type are made up of various modifications of silica: quartz, crystobalite, tridymite, vitreous material, quartz glass.

Characteristics of the thermal conductivity— temperature relationship, for single-phase (quartz glass, crystobalite, quartz) and multiphase (Dinas, highly dense Dinas, Dinasochromite) refractories were investigated to ascertain the cause of the difference in thermal conductivity of different Dinas refractories.

Some properties of the investigated materials are given in Table 13 and experimental results for the relationship of thermal conductivity with temperature are shown in Fig. 28 and in Table 14.

It was found that thermal conductivity of crystalline modifications of silica (crystobalite measurements were done on fully crystallized quartz glass, those on quartz were done on crushed quartzite) increases almost linearly with temperature. The small

60

TABLE 13

Some properties of refractory materials having high silica content

Refractory material	Chemical composition, %							Packing density g/cm^3	Apparent porosity %
	Cr_2O_3	SiO_2	MgO	Al_2O_3	Fe_2O_3	CaO	Misc.		
Dinas (I)	‒	94.12	0.15	1.22	-	-	0.24	1.91	20.1
Dinasochromite (I)	6.24	85.14	2.72	3.60	2.04	0.40	0.10	2.06	16.6
Highly dense Dinas (II)	-	96.4	0.38	1.14	1.22	0.65	0.14	2.05	13.0
Natural quartzite, crushed (III)	-	97.6	0.06	1.90	0.32	0.08	0.10		Close to zero
Natural quartzite, fused amorphous quartz (IV)	-	98.24	0.30	0.84	0.18	0.21	0.08	2.06	1.03
Lightweight Dinas (from Krasnoarmeĭsk) (V)	-	89.76	0.22	2.00	2.58	4.96	0.18	1.10	52.1
Lightweight Dinas (from Pervoural) (VI)	-	92.95	0.22	1.75	1.62	0.20	0.20	1.09	53.5
Crystobalite (III)	-	98.24	0.30	0.84	0.18	0.21	0.08	2.06	1.03*

*Taken same as in the original quartz glass

TABLE 14

Thermal conductivity of materials having high silica content, (after reduction to zero porosity, by the formula $\lambda_p = \lambda_o(1-p)$

| Refractory material	Thermal conductivity, kcal/m.h.K. at temperature K (^oC)													
	373 (100)	473 (200)	573 (300)	673 (400)	773 (500)	873 (600)	973 (700)	1073 (800)	1173 (900)	1273 (1000)	1373 (1100)	1473 (1200)	1573 (1300)	1673 (1400)
Crystallized quartz glass (crystobalite)	0.82	0.86	0.90	0.94	0.98	1.02	1.06	1.14	1.22	1.30	1.40	1.50	1.61	1.78
Quartz (natural crushed quartzite)	0.82	0.86	0.90	0.94	0.98	1.02	1.06	1.14	1.22	1.30	1.40	1.50	1.61	1.78
Quartz glass	0.92	1.00	1.08	1.18	1.38	1.68	2.00	2.38	2.88	3.50				
Dinas	1.15	1.19	1.25	1.30	1.34	1.40	1.50	1.57	1.67	1.80	1.92	2.05	2.17	2.35
Highly dense dinas	-	1.56	1.53	1.52	1.54	1.61	1.68	1.75	1.84	1.95	2.05	2.25	2.44	2.65
Dinasochromite	1.11	1.14	1.20	1.25	1.29	1.35	1.45	1.52	1.61	1.74	1.86	1.98	2.10	2.27
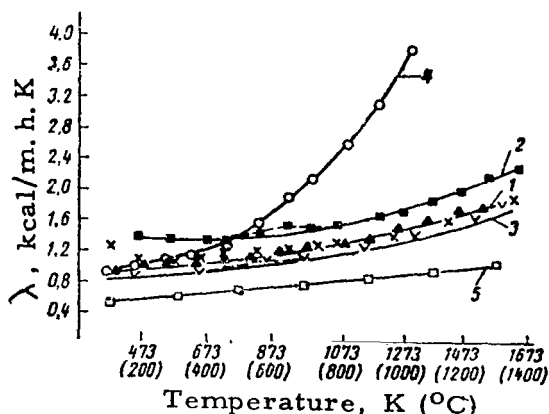
Fig. 28. *Variation of thermal conductivity with temperature, in the case of high silica-content refractories.*

1 - Dinas; 2 - highly dense Dinas and Dinasochromite; 3 - quartzite; 4 - crystobalite; 5 - quartz glass.

difference between the behaviors of quartz and crystobalite is that the thermal conductivity of quartz has a minimum between 773 to 873 K (500 to 600°C) which can be explained by the transition $\beta \leftrightarrows \alpha$ for quartz at 846 K (573°C). A similar aspect was also observed by other investigators [35] during thermal conductivity determinations of granite. Such changes, which occur around 573°C, are not detected in Dinas and Dinaso-chromite because of the small amount of quartz. The possible occurrence of this effect is further reduced on account of porosity and remains within experimental errors. Crystobalite and quartz (excluding highly porous, lightweight Dinas) have the smallest value of thermal conductivity. Considering that quartz and crystobalite contain the least amount of impurities and have a porosity close to zero, it can be surmised that such temperature characteristics appertain to materials made from modifications of pure silica. The identical results obtained for thermal conductivity of quartz and crystobalite prove that differences in the crystalline structure of silica, e.g. the shifts in the tetrahedrals SiO_4 and certain variations, displace Si—O into different modifications of silica, so that they do not affect the value of the mean free path of phonons.

It is difficult to give a rigorous treatment to the studies on thermal conductivity of Dinas which includes several modifications of silica, vitreous phase and heat conducting oxides like chromium oxide hematite. Experimentally, a higher value of thermal conductivity is obtained than for pure modifications

63

(Fig. 28). Among the various types of Dinas, the highest thermal conductivity is obtained for the highly dense and least porous Dinas containing hematite. Dinas and Dinasochromite have the same thermal conductivity although they have different porosity and chemical compositions.

It appears that for a precise understanding of the laws governing thermal conductivity variations in this case, it is necessary to investigate thermal conductivity in the two-phase system.

CHAPTER III

FACTORS AFFECTING HEAT TRANSFER THROUGH CERAMICS

1. Features of Heat Transfer Through Ceramics

A large majority of refractory insulators[1] used in industry and science are substances having a large number of connected or isolated pores.

The interest in the problems of heat transfer through powders and ceramics is due to their applications which range, on the one hand, from the highest temperatures (lining for induction furnaces) to the lowest temperatures (thermal insulation of vessels for storing cryoganic liquids and, on the other hand, from chambers exhausted to 10^{-6} mm Hg Col to various kinds of equipment with highly conducting gases like helium and hydrogen at pressures greater than the atmospheric pressure.

Such universal and, not seldom, intuitive applications of ceramics and powders, in the industry demand deeper studies on the characteristics of heat transfer through them.

A ceramic body can be considered as consisting (Fig. 29) of grains, cracks or pores (closed or connected) and contacts between the grains (formed either during baking, or mechanically). For each element of a ceramic material, there is a characteristic form of heat transfer. Two mechanisms are possible in grains: conduction and radiation. Thermal conductivity of refractory insulators, the most common of the refractories, has been discussed in the previous chapter.

---

[1] *When considering the transfer of heat by a porous material, we use the term "effective thermal conductivity", meaning thereby the total effect of heat transfer, as distinguished from the term 'thermal conductivity', usually used for compact bodies.*
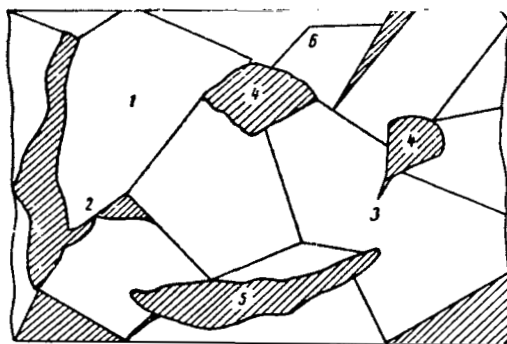
Fig. 29.Elements of a ceramic.

1 - grain of the body; 2 - contact of non-baked grains; 3 -- contact of baked grains with formation of the neck; 4 - closed pore; 5 - communicating pore; 6 - crack in the grain.

Grains, as a rule, form semicrystalline complexes, in which, according to Lee and Kingery [20], radiational heat exchange is negligibly small. Hence, heat transfer through grains is effected by conduction. Taking into account the phonon conductivity mechanism in refractory insulators, it can be said that thermal conductivity of grains decreases (except for zirconium dioxide, silica, etc.) almost directly with rise in temperature.

Three forms of heat transfer can, in principle, exist in pores and microfractures: thermal conduction of gas in pores and microfractures, convection of gases in pores and microfractures, and radiation between walls of a pore.

Instead of a contact between grains, a neck of the grain material (ceramic) as well as a mechanical contact (powder mass) could form between the grains. In the first case, the thermal conductivity through the neck between two adjacent grains of a ceramic depends on its cross section and on the gas layer around the neck. As for the mechanical contact between the grains, a contact has considerable thermal resistance, and so the thermal conductivity would be mainly realized through the gas.

All the elements of a ceramic and all the important forms of heat transfer realized under definite conditions take part in the total heat transfer in a ceramic material or powder. They result in an "effective thermal conductivity". Predominance of one or the other constituent of the ceramic and of one or the

66

other form of heat transfer depends upon the structure of the material, the temperature and the physical properties of the substance.

Some aspects of heat transfer through dispersed material have been systematically and fully discussed in the monograph [31] and in other publications. Since very little study has been done on refractory ceramics and powders from the point of view of thermal conductivity, and hardly any systematic study has been done at higher temperatures, it would be very interesting to evolve some laws of heat transfer through dispersed phase.

2. Influence of the Degree of Exhaustion within the Pores, on the Effective Thermal Conductivity of Refractory Ceramics

Thermal conductivity of refractory ceramics at pressures less than the atmospheric pressure has practical importance (for example, for using them in vacuum pouring of steel, for internal lining of vacuum type induction furnaces and in electrical resistance furnaces) and its study is necessary for an understanding of the heat transfer processes through ceramics.

Data are available in literature about the effect of vacuum on the effective thermal conductivity of powders at low temperatures (Smolukhovskiĭ effect) [32, 33] and about the variations in thermal conductivity of some refractory oxides in vacuum [34]. But the effect of the extent of exhaustion on thermal conductivity of refractory ceramics, where grains form a continuous body, has not been investigated.

Refractory materials covering a wide range of thermal conductivities (0.5 to 6 kcal/m. h. K) and porosities (approximately 10 to 50%) were selected for investigation, as these ranges completely represent the class of ceramics called refractory oxides. Thermal conductivity variations with temperature were measured by the method described in Chapter I with the apparatus placed inside a vacuum chamber of large volume (0.5 m^3). The chamber was so air-tight that it could maintain any pressure from 10^{-2} to 760 mm Hg Col during the experiments, without recourse to pumping.

The temperature — thermal conductivity characteristic at atmospheric pressure was determined in an open chamber. Thereafter, without changing the specimen, air was pumped out to the required pressure, and the characteristic was recorded. Pressures less than 1 mm Hg Col were measured with a manometric lamp Type LT-2 and a matching vacuummeter Type UTV. Pressures greater than 1 mmHgCol were measured with a mano-vacuummeter.

After recording the temperature characteristic at the minimum pressure (in our case, 10^{-4} mm Hg Col), the pressure inside the chamber was gradually increased to the atmospheric pressure and the measurements were repeated at atmospheric pressure to check the results. The results obtained (Fig. 30) for thermal conductivity variation with degree of exhaustion showed that, in a certain range of exhaustion, there is a considerable variation and an appreciable change in the character of the temperature — thermal conductivity relationship.
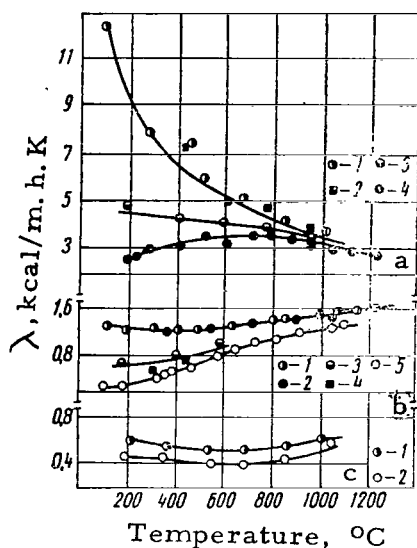

Fig. 30.Effective thermal conductivity of refractory ceramics at various temperatures, under different degrees of exhaustion.

a - for magnesite: 1 - at atmospheric pressure; 2— at 40 mm HgCol; 3 - at 4 x 10^{-1} mm HgCol; 4 - at 1 x 10 $^{-4}$ mm HgCol.

b - for Dinas: 1 - at atmospheric pressure; 2 - at 60 mm HgCol; 3 - at 4 x 10^{-1} mm HgCol; 4— at 1 x 10^{-1} mm HgCol; 5 - at 1 x 10^{-1} mm HgCol.

c - for forsterite; 1 - at atmospheric pressure; 2 - at 1 x 10^{-4} mm-HgCol.

68

A consideration of the main factors affecting heat transfer through ceramics leads to the conclusion, that the only cause of variation in effective thermal conductivity is the removal of air from the pores*. However, according to the molecular-kinetic theory of gases [40], thermal conductivity should depend on pressure when the mean free path of molecules becomes of the same order or higher than the distance between the particles between which heat exchange takes place through the gas.

In general, the free path length of gas molecules at different pressures and temperatures is:

$$\bar{\ell} = \frac{kT}{\sqrt{2\pi\sigma^2}\, p}$$ (8)

where, $\bar{\ell}$ = mean free path
  k = Boltzmann constant
  p = gas pressure
  T = Absolute temperature
  σ = molecule diameter.

Substituting the values of the constants, and considering the mean diameter of nitrogen and oxygen molecules (the main components of air) as the "diameter of air molecules",

$$\bar{\ell} = 2 \cdot 58 \times 10^{-4}\, \frac{T}{p}.$$ (9)

The mean free path of air molecules at any given temperature and pressure could be calculated with this formula.

Now consider the experimental results for thermal conductivity at various degrees of exhaustion (Fig. 30), assuming that the distance d between heat exchanging surfaces is equal to the pore diameter.

In an atmosphere of air at a pressure of one atmosphere, the thermal conductivity of Dinas (Fig. 30) at first falls by a negligible amount, but at temperatures more than T = 573 K (300°C), it increases with temperature almost linearly. At a pressure of 60 mm Hg Col, the effective thermal conductivity of Dinas retains the value and nature of the temperature characteristic of the material at atmospheric pressure. Measurements at a pressure of 4 x 10^{-1} mm Hg Col showed appre-

* i.e., intercommunicating pores.

ciable decrease in thermal conductivity. With further reduction
in pressure (4 x 10^{-1} to 1 x 10^{-4} mm Hg Col) the thermal conduc-
tivity decreases by a small amount. The pressure range in
which effective thermal conductivity decreases rapidly (60 mm
Hg Col to 1 x 10^{-1} mm Hg Col), corresponds to the range of
mean free paths: 0.13 x 10^{-2} to 0.12 mm at $27^{O}C$; 0.8 x 10^{-8} to
0.8 mm at $1500^{O}C$. According to the petrographic analysis, the
range of mean free paths 0.0013 to 0.8 mm   corresponds to the
pore sizes in a Dinas specimen (0.01 to 0.6 mm). Rigorous
comparison is difficult owing to approximations in microscopical
estimation of pore sizes, differences between the sizes of
various pores, and other factors.

A similar behavior was observed for magnesite. The
reduction of pressure to 40 mm Hg Col did not lead to a decrease
in thermal conductivity, but at 4 x 10^{-1} mm Hg Col considerable
decrease in conductivity was noticed. Further reduction in
pressure leads to very small variations in conductivity .

Moreover on the basis of these preliminary experiments,
it can be concluded that the conductivity of magnesite varies
with pressure in the low pressure range 10 to 1.5 x 10^{-1} mm
Hg Col, which corresponds to a mean free path of 0.01 to 3.0 mm
at that temperature. Petrographic analysis data gave the pore
sizes in the magnesite specimen between 0.1 to 1.8 mm. Re-
lationship between λ and log P is plotted in Fig. 31.

The effect of a rapid decrease in thermal conductivity of
the medium, filling the pores at atmospheric pressure, on the
variation of effective conductivity of the material with tem-
perature was also investigated, for a highly conducting ceramic
as well as for a highly porous (lightweight) ceramic. For this
purpose, the variation of effective thermal conductivity with
temperature was investigated in air, at atmospheric pressure
and at a pressure of 1 x 10^{-4} mm Hg Col, for several refrac-
tories having different thermal conductivities and different λ(T)
characteristics. The results obtained are shown in Fig. 32. The
computed values of the relative change in conductivity of the
studied materials are given in Table 15.

The variation in effective thermal conductivity of a cera-
mic, due to a decrease in the conductivity of the filling medium
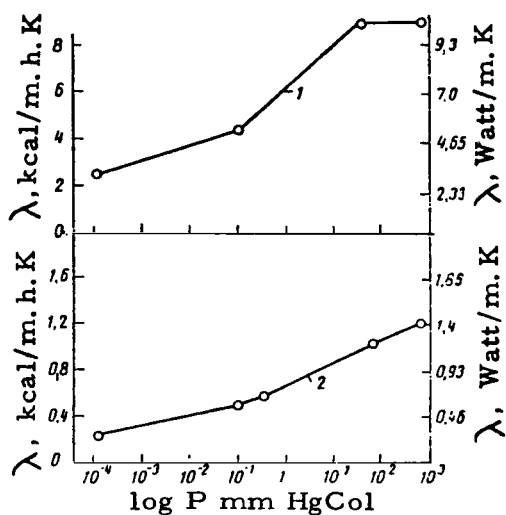of the pores, brings about the following three effects, which are

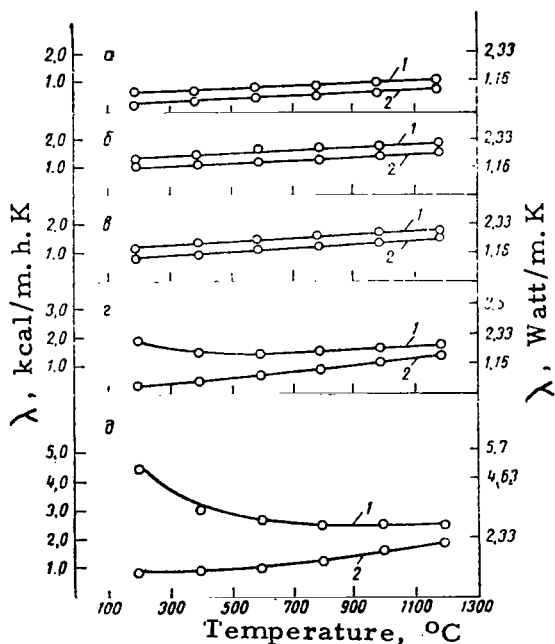Fig. 31.Variation of thermal conductivity at 200°C, under different pressures, for magnesite (1) and Dinas (2).

Fig. 32.Variation of thermal conductivity with temperature -- in air at atmospheric pressure (1), and at a pressure of 1 x 10⁻⁴ mm HgCol (2) -- for materials with different thermal conductivities and having different λ (T) characteristics. (Properties shown in Table 15).

71

TABLE 15

Relative variations in thermal conductivity (λ) of alumina-silicate refractories, at a pressure of 1 x 10^{-4} mm HgCol

Component content, %		Porosity %	Absolute value of λ in air, kcal/m.h.K	Reduction of λ in vacuum (1x10^{-4} mm HgCol) with respect to λ in air, %
Al$_2$O$_3$	SiO$_2$			
97 (e)	1.00	24	3.60* 2.40	76* 51
83.19 (d)	13.6	13.1	1.64 1.46	76 43
68.3 (c)	25.1	16.5	1.20 1.60	13 18
42.9 (b)	52.7	12.4	1.38 1.74	23 20
35.9 (a)	58.3	15.1	0.72 0.90	56 20

*The value in the numerator is for 573 K (300°C); while that in the denominator is for 1073 K (800°C).

well defined at temperatures at which the radiational heat transfer can be neglected:

a)   the greater the thermal conductivity of air inside the pores (corundum, Fig.32; magnesite, Fig.30) at atmospheric pressure, the greater is the decrease in thermal conductivity of material at a pressure of 10^{-4} mm Hg Col.

b)   for substances (corundum, Fig.32; magnesite, Fig.30)

following the $\lambda \sim \frac{1}{T}$ law at atmospheric pressure in air, this

relationship changes in the opposite direction, i.e., at maximum exhaustion an increase in thermal conductivity is observed with an increase in temperature.

For comparatively dense materials (apparent porosity 24 to 25%) in which ordinarily $\lambda \sim \frac{1}{T}$, the variation in the character of thermal conductivity-temperature relationship at a pressure of 1 x 10^{-4} mmHgCol resembles the variation in highly porous materials compared to that of dense ones (Fig. 33) and it resembles the variation in powders compared to that of baked ceramics (Fig. 36). In materials with a positive temperature relationship (see Fig. 30) (high alumina and firebrick materials, Dinas), the exhaustion of gas in the pores does not affect the temperature relationship (Fig. 34).
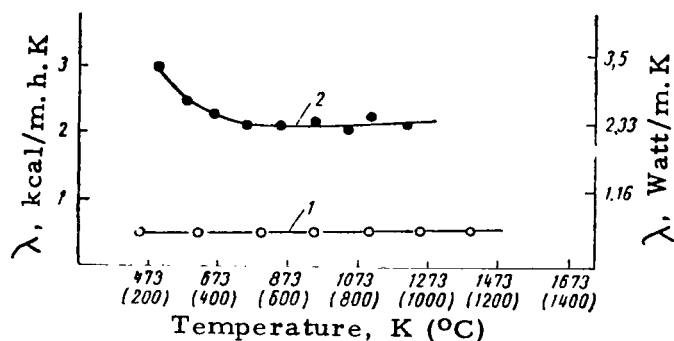

Fig. 33. *Variations of effective thermal conductivity with temperature, for high alumina - content ceramic, in the case of: dense material with porosity 17% - (1): porous material with porosity 57% - (2).*

c)   throughout the temperature range, the effective thermal conductivity of highly porous ceramics at 1 x 10^{-4} mm Hg Col decreases by 22 to 24% with respect to that at atmospheric pressure. This decrease is small in comparison with that in dense ceramics.

The reason for variation in effective thermal conductivity is that, firstly, the thermal conductivity of the gas is reduced; and secondly, the contact thermal conductivity (the component characterizing heat transfer through the gas layer around the actual contact)   varies considerably with decrease in thermal conductivity of the gas. Moreover, the decrease in thermal conductivity of air (which itself is quite low), plays an indirect role in reducing the effective thermal conductivity. This happens according to the molecular-kinetic theory, when the mean free path of the gas molecules in the ceramic becomes comparable to, or greater than, the distance between the walls of the pore through which the heat transfer takes place.
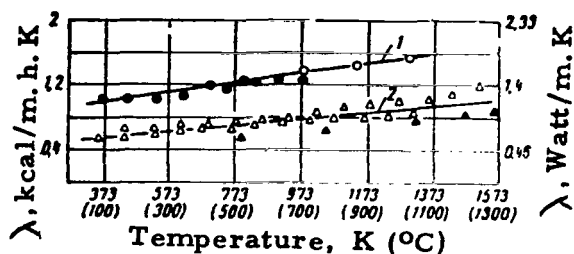
*Fig. 34.Variation of effective thermal conductivity with temperature, in the
case of ceramics with a body conductivity directly proportional to the
temperature.*

1 - Dinas; 2 - Lightweight Dinas.

The temperature relationship for materials with high λ,
but having $\lambda \sim \frac{1}{T}$, changes with decrease in the thermal
conductivity of air and so also at low temperatures when the
component due to radiational heat transfer becomes small and
the conductivity of air no more depends on the pressure.

The steep decrease in thermal conductivity of highly
conducting materials is due to the fact that the reduction in
thermal conductance of the contacts impedes the appearance of
the natural thermal properties of the ceramic (analogous to
thermal conductivity of lightweight refractories and powder
mass), because of the reduction in effective cross section for
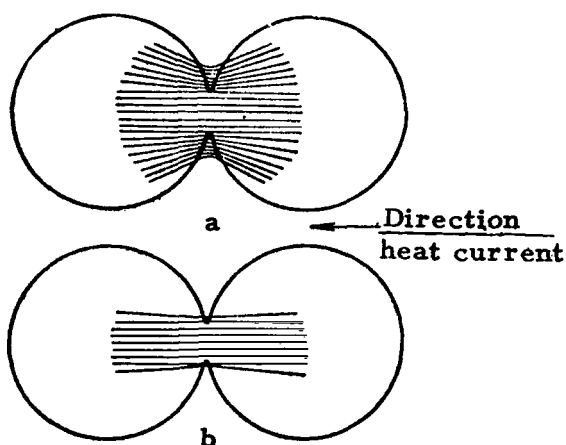heat flow (Fig. 35).

*Fig. 35.Diagram of heat flow through ceramics, at normal pressure in the
pores -- (a), and under a vacuum of about 1×10^{-4} mm HgCol --(b).*

74

In highly porous (lightweight) ceramics, appreciable decrease in contact thermal conductivity does not take place and therefore, such a ceramic has a minimum reduction in the effective thermal conductivity (see Figs. 30, 32). At high temperatures (1073 to 1273°C), the temperature relationship curves, under standard conditions (760 mm Hg Col.) and in vacuum, for corundum, Dinas, magnesite and some high alumina-content materials are quite close (Figs. 30, 31). This obviously shows that, in the heat exchange at contacts, the conductivity involves a radiation component for heat transfer through the gas layer surrounding the actual contact. The contact thermal conductivity, due to the thermal conductivity of gas in the pores, decreases with temperature rise for substances having $\lambda \sim \frac{1}{T}$ but it changes less noticeably in materials having $\lambda \sim T$ (Table 16).

TABLE 16

Variation of contact thermal conductivity of refractory ceramics
with temperature

Substance	Apparent porosity %	Value of contact thermal conductivity, kcal/m.h.K at mean temperature K (°C)					
		473 (200)	673 (400)	873 (600)	1073 (800)	1273 (1000)	1473 (1200)
Magnesite	25.3	6.5	3.5	1.7	0.7	0.4	0.60
Corundum	24.0	3.54	2.07	1.58	1.22	0.90	0.60
Dinas	24.5	0.95	0.65	0.55	0.30	0.30	0.60

It is clear from the observed data that the effect of reduction of pressure in ceramic pores is due to the same molecular-kinetic effects as in powders (Smolukhovskiĭ effect [32]). Nevertheless, qualitatively they are more varied, particularly regarding the character of the temperature relationship. These effects enable us to appreciably change the thermophysical properties of ceramics and their temperature relationships over quite a wide range.

The relationship of effective thermal conductivity with the degree of exhaustion could be utilized to improve the thermal properties of refractory ceramics.

3. Effect of Actual Particle Contact on the Effective Thermal Conductivity of Dispersed Refractory Material

Contact thermal conductivity, according to U. P. Shlykov and E. A. Ganin [36 to 38], is the sum of thermal conductivities due to actual contact and due to the gas layer around the contact.

The effect of the degree of exhaustion and of the gas layer around the contact, on the effective thermal conductivity, was dealt with in the preceding section. The difference between a powder mass and a pressed, baked ceramic of the same materials, having the same porosity, is only that in the first case the grains contact each other without baking and in the second case the grains are baked, forming a neck contact in the grain material. By measuring thermal conductivity of powders and specimens baked from them, the effect of the baking of grains on thermal conductivity could be determined, i. e., the role of factual contact on the heat transfer through ceramics can be determined.

The apparatus described above was used over a wide range of temperatures, for measuring the thermal conductivity up to 1773 K (1500°C) for ceramics and a modified version was used for powders. In both the cases, the test cylinders had approximately the same size. For ceramics, the cylinder had a height 200 mm, outside diameter 75 to 80 mm; whereas the powder was filled in a hollow cylinder of height 203 mm, outside diameter 91 mm.

The materials investigated were: magnesite with 2% ZrC, magnesite on spinel bond; periclase-forsterite and periclase-spinel two-phase combination. The results of investigation are shown in Fig. 36.

For the ceramic specimen made from powder with grain size 1 to 0.2 mm, the temperature relationship retains the character of the parent material (Fig. 36) in spite of the quite high porosity (45 to 60%). At lower temperatures, the $\lambda \sim \frac{1}{T}$
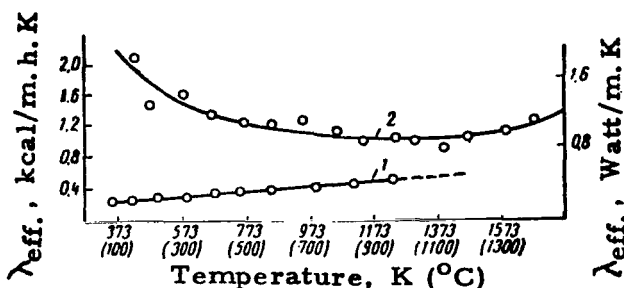
Fig. 36. *Thermal conductivity of periclase-spinel, two phase system.*
1 - powder with grain size 1 to 0.2 mm, packing density 1.2 g cm⁻³;
2 - ceramic made from powder of grain size 1 to 0.2 mm, packing density 1.9 g cm⁻³.

relationship is observed more or less clearly; at higher temperatures the effect of radiation through pores changes the λ - temperature relationship appreciably. A powder with grains, equal to the grains of the ceramic, had an effective thermal conductivity lower than that of the ceramic but the temperature relationship had the opposite sign. Maximum decrease in thermal conductivity is observed at the lowest temperatures. With increase in temperature, the difference in the effective thermal conductivity of a powder and its ceramic decreases.

In general, the grain contact area for powders is small due to the irregularity in grain shape, and has a quite high hardness value and low ductility. In other words, thermal resistance at the point of grain contact is so large due to the negligibly small contact area that the grains are disconnected as far as heat transfer is concerned. Therefore, other features of the ceramic, i.e., the conductivity of the gas in the pores and around the contact are mainly important in this case. Conductivity of the gas in the spaces around the powder grains affects to a much less extent and so the effective thermal conductivity in this case is small.

In the ceramic specimen, where the grains form a continuous body, a neck is formed in the contacts due to baking, which has a grain size comparable to that of the grain itself. In this case the conductivity of the body increases due to heat exchange through the gas layer around the actual contact and forms the major part of the effective thermal conductivity.

Experiments show that the temperature relationship of thermal conductivity of ceramics from magnesite and periclase-

77

spinelide with a porosity up to 60% has the same character as
that of the dense samplesof the same materials with zero poro-
sity [3]. At temperatures above 673 K, the proportion of contact
thermal conductivity is somewhat reduced due to an increase in
radiational conductivity. Nevertheless, these aspects cannot be
treated separately, because the radiation in the contact zone
considerably increases the contact thermal conductivity.

Even at the highest temperature considered in these
investigations, the effective thermal conductivity of powder is
just 0.53 to 0.63 that of the ceramic, only because of the
difference in thermal conductivity of the actual contact. For
zirconium dioxide powder and the ceramic made out of it, the
corresponding ratio of the effective thermal conductivities is
different from the one described above (Fig. 37). In this case,
there is practically no difference between the effective thermal
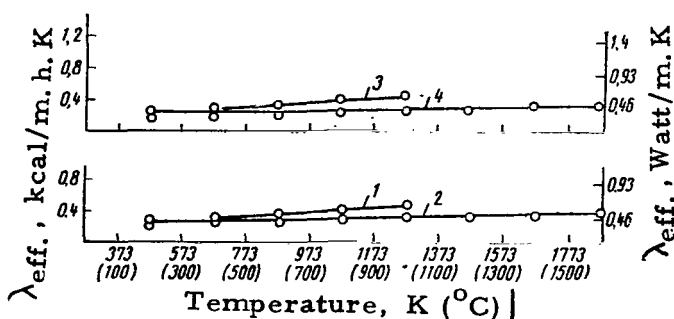conductivity of powder and ceramic, throughout the temperature
range.

Fig. 37. Thermal conductivity of zirconium dioxide stabilized with calcium
dioxide.
1 - powder with grain size < 0.2 mm, density of loose material
2.93 g cm^{-3}; 2 - ceramic from powder with grain size < 0.2 mm,
packing density 2.96 g cm^{-3}; 3 - powder with grain size 1 to 0.2 mm,
density of loose material 2.30 g cm^{-3}; 4 - ceramic from powder with
grain size 1 to 0.2 mm, packing density 2.53 g. cm^{-3}.

Two aspects have to be taken into account while consider-
ing the effect of contact thermal conductivity on the effective
thermal conductivity: a) the difference, of about one to one-and-
a-half orders, in the absolute values of thermal conductivity
for periclase-spinel, periclase-forsterite, magnesite and spinel-
bonded magnesite on the one hand and zirconium dioxide on the
other; b) the difference in the character of temperature relation-
ship.

78

The body thermal conductivity of zirconium dioxide is so small (1.5 kcal/m.h.K) that it differs by less than one order from that of the powder (0.25 kcal/m.h.K) and from the contact thermal conductivity. For the rest of the materials, effective thermal conductivity of the powder (0.25 kcal/m.h.K) is less than that of the body by at least 2 orders.

The law of variation for phonon conductivity above the Debye temperature, when $\lambda \sim \dfrac{1}{T}$ holds good, applies for a majority of refractory oxides (except zirconium dioxide, glass, silica and a few others). Consequently, the variations in effective thermal conductivity for periclase-spinel, periclase-forsterite and magnesites, with reduction in grain contact cross sections and simultaneous change in temperature characteristics have a general nature.

A qualitative similarity can be observed between the variation of effective thermal conductivity with decrease in conductivity of actual contact and thermal conductivity of gas layer around the contact, by a comparison of results of this section with those of Section 2. Fig. 38 shows the variation of
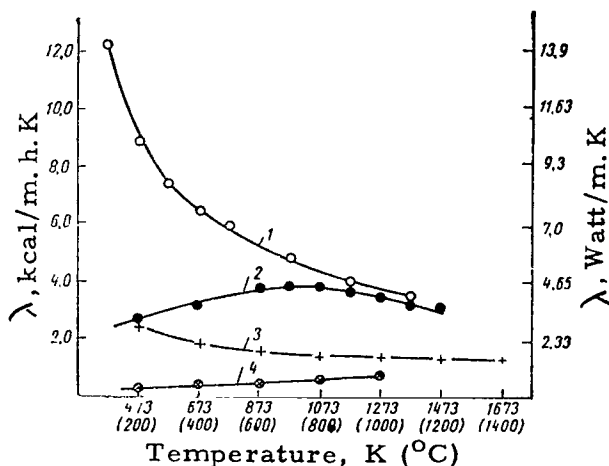

Fig. 38. *Variations of thermal conductivity with temperature, for different types of magnesite ceramics.*

1 - ceramic of porosity 24%, at atmospheric pressure; 2 - the same under a pressure of 1×10^{-4} mm HgCol; 3 - highly porous (light-weight) ceramic of porosity 60%; 4 - powder with compactness 60%.

thermal conductivity with temperature, for magnesite ceramics with different contact thermal conductivities determined by the

experimental conditions. The following ways of increasing (or regulating) thermal insulation properties of refractory ceramics are available: a) increasing the porosity; b) decreasing the thermal conductivity of gas in the pores by establishing a known vacuum in the pores; c) decreasing the area of actual contact by substituting powder for ceramic; d) decreasing the conductivity of gas in empty spaces between the powder grains. This question is not being dealt with by us, though investigations [41] indicate that the effective conductivity of quartz powder is reduced in vacuum.

4. Influence of Highly Conducting Gas on the Effective Thermal Conductivity of Refractory Ceramics

Experiments in which thermal conductivity of gas in the pores was reduced by at least three orders were discussed in the previous section. Such a reduction completely changes the picture of heat transfer through ceramics. Actually, at a pore size not more than 1 mm, only the thermal conductivity of the "body" takes part in heat transfer, while the contact conductivity through the layer of gas around the contacts and the radiation across it does not play any role at all.

Experimental results, under conditions in which conductivity of the gas in the pores was increased to seven times that of air, are discussed in this section. The measurements were conducted in the following order: the apparatus, ready for investigations, was placed in the vacuum chamber and the electrical leads and the measuring circuit were connected at the vacuum inlets. The λ (T) relationship was studied at atmospheric pressure and then at a pressure of 1×10^{-4} mm Hg Col. Thereafter, λ (T) was measured on the same setup, in a hydrogen atmosphere at a pressure of 1 atm. For this, the vacuum chamber, evacuated to 1×10^{-4} mm Hg Col, was filled with hydrogen. As the temperature increased, the excess hydrogen was let out through a water seal (in order to keep the pressure inside the chamber constant). Results of the investigations are given in Fig. 39. It also shows for comparison, the temperature relationship curves at a pressure of 1×10^{-4} mm—Hg Col. When the pores are filled with hydrogen, the thermal conductivity increases; the λ (T) curves with hydrogen and with air in the pores, both at atmospheric pressure, are parallel, barring a few exceptions (Fig. 39 c, d). At a mean tem-
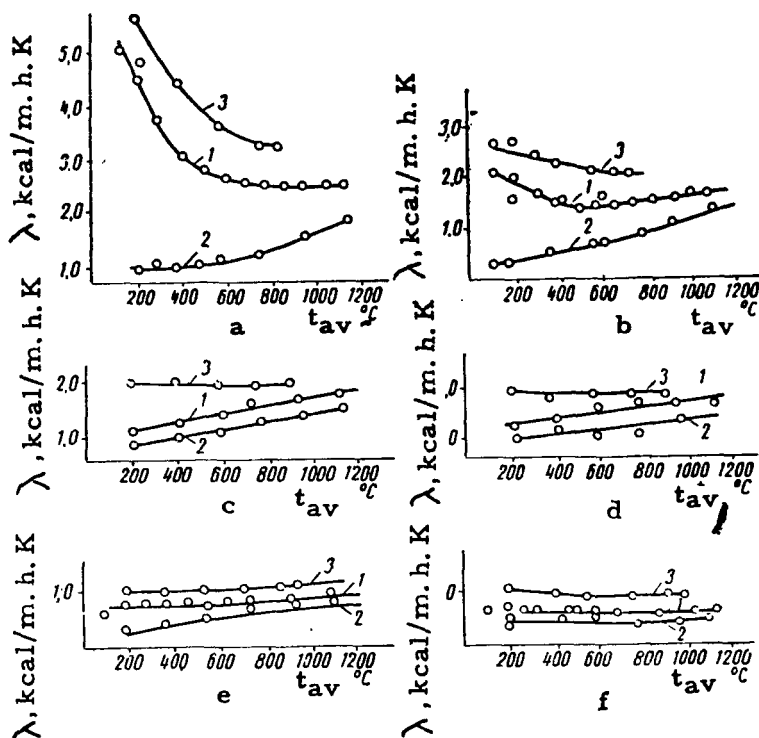
Fig. 39.*Effective thermal conductivity of refractory ceramic in air, hydrogen and vacuum.*

	a	b	c	d	e	f
apparent porosity, %	24	12.7-13.5	10-15	10-12	15.5	57.6
Al_2O_3 content, %	97	82.2	63	45	37	82

1 - in an atmosphere of air at atmospheric pressure; 2 - in an atmosphere of air at a pressure of 1×10^{-4} mm HgCol; 3 - in an atmosphere of hydrogen at atmospheric pressure.

perature of 1073 K (800°C), the thermal conductivity increases by 17 to 35% for a porosity of 10 to 20%, and by 60% for a porosity of 60%. This change, when the pores are filled by hydrogen, is explained by the higher thermal conductivity (about 7 times) of the hydrogen.

Using the additive formula, which holds good when the gas phase fills isolated spherical pores,

$$\lambda = C_1\lambda_1 + C_2\lambda_2 \tag{10}$$

(C_1, C_2 being the concentrations of the phases; λ_1, λ_2, their thermal conductivities) and calculating λ when hydrogen fills the ceramic pores, the following results were obtained: The

81

less the thermal conductivity of the specimen (within a range of 10% of the thermal conductivity of the "body"), the closer is the calculated value to the experimental value (the experimental values are in fact somewhat higher than those estimated). For a mean temperature (1073 K, i. e., 800°C), the excess of experimental values over the estimated ones is as follows:

kcal/m. h. K	3. 14	2. 00	1. 94	1. 10	1. 00
(excess) %	25	32	16	14	10

A similar divergence was observed by Wygant and Crowley [42] while determining thermal conductivity of concrete insulation, at temperatures up to 673 K (400°C), in hydrogen and helium atmospheres. Theoretical formulae of Russell [43] and Loeb [44], agree well with these experimental results only in the case of materials of low thermal conductivity and open pores. For materials with closed pores (on which our experiments were done), except in the case of high alumina-content lightweight refractory, the formulae are good enough only at pressures above the atmospheric pressure.

The divergence between experimental and theoretical values could be due to the fact, that the share of contact conductivity through the gas phase around the contacts is not accounted for anywhere. When pores are filled with hydrogen, the contact thermal conductivity is more than when they are filled with air. (This is also the case, when the pores contain air rather than vacuum.). Contact thermal conductivity is determined by the thermal conductivity of the gas in the pores as well as by the thermal conductivity of the "body".

Thus, the theoretical formulae of Loeb [44], Russell [43] as well as the additive formula used by us do not fully take into account the real structure of the ceramic and the complete heat exchange process through it.

Experimental results obtained, on changing the effective thermal conductivity by filling the ceramic pores with more conducting gas, show that the increase in λ is not much for dense materials, but it is quite large for porous ones.

As such, the use of highly conducting gases (helium, hydrogen) in conjunction with insulation ceramic adversely

affects the performance of the ceramic. In such cases, dense materials with low thermal conductivity are more effective. The character of λ (T) in certain cases is somewhat changed (Fig. 39 c, d) at lower temperatures, due to better heat exchange through the gas layer around the contact.

5. Effective Thermal Conductivity of Refractory Powders

Refractory powder insulation is widely used in consideration of its special characteristics: i) the possibility of insulating the spaces of complicated shapes and ii) a minimum of effective thermal conductance (as compared to a ceramic having the lowest thermal conductivity). However, for correct choice of the insulating powder and its size, a knowledge of the factors affecting the effective thermal conductivity is essential. Refractory powders of zirconium dioxide, magnesite with zirconium dioxide additive, magnesite on spinel bond, periclase-forsterite, periclase-spinel, having grain size of 2 to 5 mm, 1 to 0.2 mm and less than 0.2 mm, were studied. The variation with temperature, of the effective thermal conductivity of the powders of all grains sizes was studied at the hot face temperatures of 473 to 1473 K (200 to 1200°C). The results are shown in Fig. 40 and could be summed up as follows: (i) Variations in effective thermal conductivity of powders do not depend on the type of material (at least up to 1273 K (1000°C) but depend only on the grain size. (ii) At 373 to 473 K (100 to 200°C), the effective thermal conductivity does not depend even on the grain size and is equal to 0.2 kcal/m. h. K (0.23 Watt/m. K) or, it may be that the difference in conductivity of different powders is less than the sensitivity of the method used. (iii) The small value of effective thermal conductivity at low temperatures could be explained by the action of two processes, which have little effect from the heat exchange point of view, viz, the heat transfer through the grain contacts and the thermal conductivity of air in the empty spaces. However, both these processes are interrelated and the total effect becomes as much as 0.2 kcal/ m. h. K, even though the thermal conductivity of air at these temperatures is smaller by one order (Fig. 39). Thus the air in the empty spaces between grains affects the value of effective thermal conductivity. The experiments [32] and the measurements [41] showed that with decrease in gas pressure in the empty spaces, the effective thermal conductivity of powders could decrease to one-tenth the normal value.
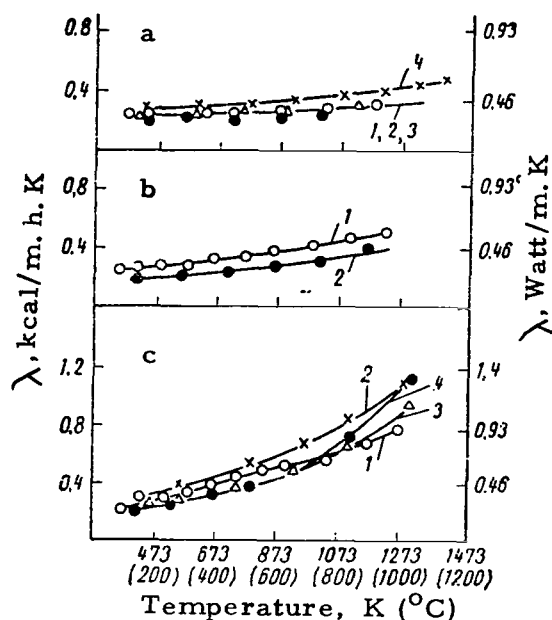
Fig. 40. *Effective thermal conductivity curves for refractory powders.*
*a - grain size < 0.2 mm; b - grain size, 1 to 0.2 mm; c - grain
size, 2 to 5 mm.*

*1 - periclase-spinel combination; 2 - periclase - forsterite combina-
tion; 3 - magnesite on spinel bond; 4 - magnesite with 2% zirconium
dioxide.*

Since the above experiments show that the effective ther-
mal conductivity of powder does not depend on grain size, it
appears that the contact thermal conductivity plays a minor role.
Consolidation of powder having grain size smaller than 0.2 mm,
leads to an increase in powder density by 20% and that of 10%
in thermal conductivity. This confirms that the possible effect
of contact thermal conductivity on effective thermal conductivity
is negligible compared to the effect of gas in the empty spaces.
This is also shown by experiments on the effect of porosity of
the grains themselves. Effective thermal conductivity of dense
powders and those of 60% porosity was measured to check up
this point. It was found that there is practically no difference
in effective thermal conductivity of the lightweight and the dense
powders having grain size less than 0.2 mm -- apparently
because, the structure of the powdered mass remains approxi-
mately the same up to this grain size. With an increase in the
grain size and also with increase in temperature, the difference
between effective thermal conductivity of porous and dense
powders reached up to 10%.

At temperatures $>$ 573 K (300°C), grain size affects the thermal conductivity. The temperature relationship of conductivity, i.e. λ (T), also depends on grain size. For powders of grain size $<$ 0.2 mm, the effective thermal conductivity increases linearly with temperature. It is peculiar that the straight line, representing thermal conductivity, is parallel to the temperature relationship for air throughout the temperature range, and is above it by one order. It can be concluded from this comparison that, radiational conductivity is absent in a powder mass having grain size less than 0.2 mm and porosity $\sim$ 10%, while the spaces between the grains can be assumed to have the same dimensions as the grain. This conclusion is of practical importance, and is also valid for ceramics. For powders, with grain size 1 to 0.2 mm, the curve has a steep gradient, and it is more so for 2 to 5 mm. In these cases, the effect of radiational conductivity on effective conductivity is considerable. The radiational conductivity, at 373 to 1473 K (100 to 1200°C), of powders having grain size 2 to 5 mm is close to and in some cases even greater than the thermal conductivity of many refractory ceramics. The use of powders having this grain size is therefore not desirable. At the same time, operational characteristics of powders having small grain size are bad on account of increased susceptibility to thermal disintegration, formation of settling cracks and consolidation. On the other hand, operational characteristics are quite promising for powders having grain size 2 to 5 mm. Hence the possibility of reducing inter-grain spaces by using a mixture of powders of different sizes was verified. It was assumed that the smaller grains (1 to 2 mm) fill the space between the bigger grains (2 to 5 mm), and thereby reduce the total volume and hence the radiational thermal conductivity. A mixture consisting of 55% of 2 to 5 mm powder and 50% 1 to 0.2 mm was taken. Effective thermal conductivity of such a mixture was close to that of the smaller grains, i.e., the dimensions of the spaces can consider-ably improve the thermal insulation properties of the powder and ceramic by creating a structure which would nullify the action of the effective heat transfer processes: radiation, phonon conductivity, conductivity of the grains and the body.

6. Influence of Porosity, Shape and Dimensions of Pores on Effective Thermal Conductivity of Ceramics

The existing formulae connecting thermal conductivity and porosity of refractories, (except the modified formula [45]) do

not take into account the radiation through pores and spaces. Till now, contact thermal conductivity has not been included in such calculations. General theoretical consideration of this aspect is also important due to the fact that the relationship $\lambda(T)$ has been little studied experimentally, particularly in a wide temperature range. Some results of experimental investigations on the effect of porosity on effective thermal conductivity of refractory ceramics are given in this section.

The variations of thermal conductivity with temperature for two corundum ceramic structures are shown in Fig. 41.

In respect of porosity (80 to 82.5%) and content of Al_2O_3 (95.5 to 96%) and SiO_2 (3.10 to 3.40%), these two ceramics are almost identical. The shape of pores in both the ceramics is round, and the pores are closed. On an average, the pores of the one are twice the size of those in the other. In the ceramic with bigger pores, the pore size is more than the minimum size (around 1 mm) at which radiational conductivity is just detectable. For this ceramic, the number of contacts between grains, in a plane perpendicular to the heat flow, would be as many times less as the difference in the mean pore diameters, i.e. two times.

This led to a steep fall in conductivity at low temperatures (up to 700°C), as a result of the increase in pore sizes, reduction of curvature in the baked contact zone and, consequently, of the sharp decrease in contact thermal conductivity through the gas layer around the actual contact (see Fig. 34). Because of this, the effective thermal conductivity at lower temperatures is more for the ceramic with smaller pores. For the low-porosity ceramic with high contact thermal conductivity, the relationship $\lambda(T)$ has the same character as that of the ceramic body material.

At temperatures above 700°C, the curves of the effective thermal conductivity values of the two ceramics change considerably. It appears that radiational conductivity is absent in the ceramic with pore sizes 0.3 to 0.9 mm (curve 1) and that λ decreases right up to 1673 K (1400°C). On the other hand, radiational conductivity in the ceramic with pores 0.6 to 1.4 mm becomes so high, that the character of the temperature relationship is changed. At 1473 K (1200°C), the thermal conductivity of the ceramic with large pores does not appreciably differ from

that of the ceramic with smaller pores, although the former was found to be twice as much as the latter at 373 K (100 ℃).

The effect of the shape of pores on the thermal conductivity of high alumina-content materials was also studied. A sharply defined region of porosity of about 10% was selected. The materials did not practically differ from one another in porosity and chemical composition, but the shape of pores was different. Judging from water permeability, i.e., from the rate of rise of water in a block of the test material, the pores appeared to be closed and narrow in one case (Fig. 41 a, curve 1), since the resistance to the seepage of water was large (1.72 mm/min) and the sample was found to be dense on microscopic examination.
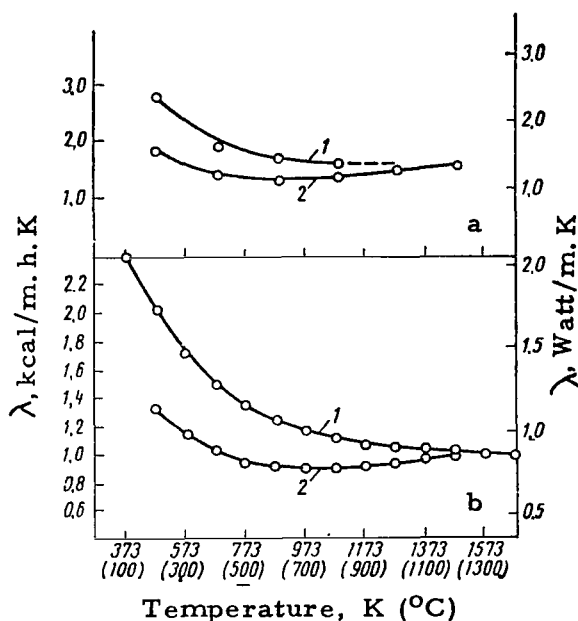

Fig. 41. *Variation of thermal conductivity with temperature, in the case of refractory ceramics with different porous structures.*

a - High alumina-content, dense ceramic:

1 - porosity, 10%; 82.8% Al_2O_3; water permeability, 1.72 mm/min.
2 - porosity 9.4%; 83.2% Al_2O_3; water permeability, 9.2 mm/min.

b - Highly porous corundum ceramic:

1 - porosity, 80%; 95.5% Al_2O_3 + 3.10% SiO_2; dominant size of pores, 0.3 to 0.9 mm; 2 - porosity, 82.5%; 96% Al_2O_3 + 3.40% SiO_2; pore size 0.6 to 1.4 mm.

In the other case (Fig. 41 a, curve 2), water permeability was large (9.2 mm/min), the ceramic was porous and the resistance to heat flow through the pores was more. Due to this difference in porosity, the denser ceramic had a larger thermal conductivity at low temperatures than the porous one. As a result of radiational conductivity, the increase in conductivity with rise in temperature is proportional to T^3 in the case of the porous structure, and so long as the dense structure conformed to the relationship $\lambda \sim \frac{1}{T}$, the difference in thermal conductivities of the two materials almost vanished; but opposite characteristics were observed in the case when $\lambda \sim (T)*$.

The following conclusions could be drawn from the above results which show appreciable change of thermal conductivity with the shape and size of the pores:

(1)   at low temperatures (up to 600 to 700°C), other conditions remaining the same, the ceramic with smaller pores has a greater thermal conductivity.

(2)   at higher temperatures (above 600 to 700°C) the ceramic with larger pores (above 1 mm) has a greater thermal conductivity.

This demarcation is due to the dominant action of different modes of heat transfer in the same temperature range in two cases. This means that under low temperature conditions of operation, the insulation with large pores is more effective and at high temperatures, the insulation with pores smaller than 1.0 mm**, (which eliminate radiational conductivity through the pores) is undoubtedly better.

Different thermo-physical properties and characters of the temperature relationship of ceramics at low (100 to 700°C) and high (700 to 1400°C) temperatures necessitate the use of two types of ceramics (high-temperature and low-temperature) depending on the temperature of operation. Such differential

---

* *The distribution of pores according to sizes also affects the effective thermal conductivity, but determination of the character of distribution is quite difficult and was not undertaken in the present investigation.*

**Precise value of pore size, above which the radiational conductivity dominates at high temperatures, is difficult to establish due to heterogenous structure of ceramics.*

application of ceramics would considerably improve the effectiveness of refractory insulation.

Two types of refractory ceramics were selected for experimental investigation of the relationship λ(p), (where p refers to percentage porosity). They had different values of thermal conductivity and different λ(T) relationship. The two ceramics were: a) high alumina-content alumina-silicates with an approximate relationship $\lambda \sim \dfrac{1}{T}$ and a thermal conductivity of the body material 2.6 kcal/m.h.K; b) firebricks of alumina-silicates, for which $\lambda \sim T$ and thermal conductivity is around 0.9 kcal/m.h.K.

The λ(p) relationship at 473 K (200°C) for high alumina-content materials and firebricks is shown in Fig. 42, a and b, respectively. The temperature chosen was low, in order to exclude to a minimum the possible radiational heat transfer effects, which distort the character of the relationship.
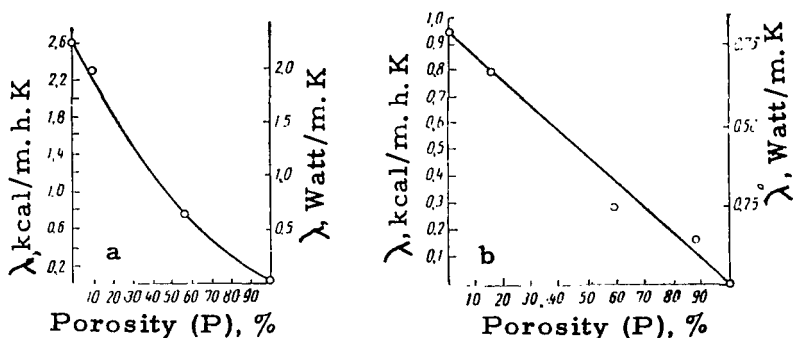

Fig. 42.Relationship of thermal conductivity with porosity at 473 K (200°C).
a - for materials with high alumina-content; b - for firebrick.

The value of thermal conductivity decreases linearly with increase in temperature for low-conducting firebricks. This means that throughout the porosity range

$$\lambda(p) = \lambda_o (1 - p) \tag{11}$$

where, λ_c = thermal conductivity of the ceramic body;

p = porosity.

For high alumina-content materials, the character of the λ(p) relationship is nonlinear.

89

CONCLUSIONS

A large majority of refractory materials consist of refrac-
tory oxides, which are heat insulators (refractory dielectrics).
The variations of thermal conductivity in these materials follow
the laws of thermal conductivity of non-conducting crystals and
their system.

Experimental investigations on the thermal conductivity of
refractory insulators show that two groups of substances can be
distinguished, according to the nature of variation of thermal
conductivity, at temperatures above room temperatures (and
particularly, above the Debye temperature).

One group of substances (MgO, Al_2O_3) has a relationship
close to $\lambda \sim \frac{1}{T}$, up to 1273 to 1473 K (1000 to 1200°C), at
which the mean free path of phonons becomes equal to the inter-
atomic spaces. Then λ is constant right up to the melting point.
The other group (quartz; zirconium dioxide; zirconates of barium,
calcium; and strontium) is characterized by $\lambda \sim T$, in the range
373 K (100°C) to the melting point. A substance of this type is
also characterized by a low value of λ_{max} at low tem-
peratures (10 K), and a λ_{min} (around 300 K), as well as by low
Debye temperature (around 250°C).

Substances of the type Al_2O_3 and MgO, on the other hand,
have a relatively high λ_{max} (6 times more than that of quartz),
a higher temperature for λ_{max} (50 K for Al_2O_3; 110 K for
BeO); a λ_{min} (1300 to 1500 K) and Debye temperatures of 800 K
for MgO and 750 K for Al_2O_3, which are far higher than that of
quartz.

It is possible to get refractory insulators having a thermal
conductivity different from that of pure substances, by forming
multi-component, multi-phase systems or solid solutions.

90

In very simple cases, it is important to distinguish between a solid solution and a two-phase system: a) formed by two insulators of the first group, for each of which $\lambda \sim \frac{1}{T}$; b) formed by two insulators of the second group, for each of which $\lambda \sim T$; c) formed by two components, one of which has $\lambda \sim \frac{1}{T}$ and the second has $\lambda \sim T$.

It has been shown, by investigating the binary system Al_2O_3 - SiO_2, that for a mixture of components differing greatly in thermal conductivity, of which one has a thermal conductivity corresponding to a mean free path equal to the interatomic distance at lower temperatures (100 to 200°C) and in which $\lambda \sim T$, the curve of thermal conductivity vs. concentration has a markedly unsymmetric character and does not have the characteristic minimum of solid solutions.

It has been shown by the example of thermal conductivity for two-phase system crystalline silica -- quartz glass, at 373 to 673 K (100 to 400°C), that for two components of equal conductivity, and a mean free path of the same order as the interatomic distance, the thermal conductivity does not vary throughout the concentration range.

In the higher temperature range for the quartz -- quartz· glass system, in which one of the components has a thermal conductivity several times larger than that of the other, and in which for one of the components $\lambda \sim T$ while that for the other $\lambda \sim T^n$ ($n \geqslant 3$), the thermal conductivity varies nonmonotonically from λ_{glass} to λ_{quartz} with changes in concentration.

It has been shown experimentally, that the minimum thermal conductivity values of refractory insulators, observed at temperatures close to room temperature, are roughly equal to 1 kcal/m.h.K for substances having $\lambda \sim T$; whereas above 100°C, for substances having $\lambda \sim \frac{1}{T}$, the thermal conductivity is equal to 5 kcal/m.h.K. Thus, from the point of view of thermal insulation properties, refractory insulators and their compounds have relatively high thermal conductivity. Moreover, a reduction in thermal conductivity and the control of thermal properties is possible by using the required structure for ceramic and powder mass.

A wide variation in effective thermal conductivity is possible in refractory ceramics by utilizing different factors, which

affect thermal conductivity. As shown in this brochure, these methods are: a) evacuation of ceramic pores; b) filling the pores with gases of different thermal conductivity; c) creation of a porous structure with pore size either smaller or greater than the limit at which radiational heat exchange is possible; d) regulation of contact thermal conductivity through the actual contact as well as through the gas layer around the contact.

The indicated possibilities are realized to a greater or smaller extent, depending on the type of the refractory insulator. In the case, when a ceramic body represents an insulator of the first group (for which the thermal conductivity in the temperature range $0^{\circ}C$ to melting point is inversely proportional to temperature), the methods of improving thermal insulation properties of refractory ceramics at lower temperatures (up to 700 to $800^{\circ}C$) are quite effective. For ceramics made from insulators, for which $\lambda \sim T$, the effect of these methods is somewhat lower in a wide range of temperatures.

It has been shown, that while estimating the effective thermal conductivity of refractory ceramics, it is essential to know not only the composition and porosity, but also the dominant pore size, i.e., the microscopic structure of porosity. This is necessitated by the fact that the action of the porous structure is not unique. If pores of large size (specially if the size is more than 1 mm) predominate in the ceramic, then at low temperatures the thermal conductivity of such a structure is quite low and a variation in the character of the temperature relationship is possible. Under these conditions, at the lower temperatures, a ceramic with large pores has an advantage over that with small pores. But, at temperatures above 873 to 1073 K (600 to $800^{\circ}C$), the thermal conductivity of coarse-grained ceramic increases due to radiation and the thermal insulation properties of the ceramic, having large pores, deteriorate.

If such pore sizes predominate in the ceramic, which avoid radiational heat exchange, then $\lambda(T)$ relationships for the ceramic and the body material are similar.

Investigation on thermal conductivity of different crystalline modifications of silica showed,that differences in the crystalline structure of the type of shifts in tetrahedrals SiO_4,and certain variations of distances $Si-O$ do not have any appreciable effect on the phonon dispersion.

LITERATURE

1. Kirillin, V.A., Problemy teplofiziki vysokikh temperatur
    (Problems of high temperature thermophysics). Vestnik
    AN SSSR, 1963, No.2.

2. Pustovalov, V.V., Teploprovodnost' ogneuporov i smez-
    hnye voprosy (annotirovannaya bibliografiya) (Thermal
    conductivity of refractories and connected problems) (anno-
    tated bibliography). NTB UNIIOgneuporov, Khar'kov,
    1960.

3. Kingery, W.D., I. Francl, R.L. Coble, T. Vasilos,
    Thermal conductivity, X. Data for several pure oxide
    materials, corrected to zero porosity. Journ. Amer.
    Ceram. Soc., 1954, 37, No.2, part II.

4. Adams, M., Thermal conductivity: III, Prolate Spheroidal
    Envelope Method, Data for Al_2O_3, BeO, MgO, ThO_2 and
    ZrO_2. Journ. Amer. Ceram. Soc., 1954, 37, No.2,
    Part II.

5. McQuarrie, M., Thermal conductivity: V. High-tem-
    perature method and results for alumina, magnesia and
    beryllia from 1000 to 1800°C. Journ. Amer. Ceram. Soc.,
    1954, 37, No.2, part II.

6. Pirogov, A.A., Penolegkovesnye ogneupory iz dvuokisi
    tsirkoniya dlya vysokotemperaturnoi izolyatsii (Lightweight
    foam refractories from zirconium dioxide for high tem-
    perature insulation). Ogneupory, 1962, No.6.

7. Ioffe, A.V., A.F. Ioffe, Teploprovodnost' poluprovodnikov
    (Thermal conductivity of semiconductors). Izv. AN SSSR,
    org. fiz., 1956, XX, No.1.

8. Krzhizhanovskiĭ, R. E., Sootnoshenie mezhdu fononovoĭ i elektronnoĭ dolyami teploprovodnosti v stalyakh (Relationship between phonon and electron parts of thermal conductivity for steels). ZhTF, 1959, XXIX, No. 4.

9. Ivanov, V. E., V. V. Lebedev, O sootnoshenii mezhdu fononovoĭ i elektronnoĭ dolyami teploprovodnosti v stalyakh (On the relationship between phonon and electron parts of thermal conductivity in steels). ZhTF, 1962, 13, No. 4.

10. McQuarrie, M., Thermal conductivity. V. High-temperature method and results for alumina, magnesia, and beryllia from 1000 to 1800°C. Journ. Amer. Ceram. Soc., 1954, 37, No. 2, part II.

11. McQuarrie, M., Thermal conductivity. V. High-temperature method and results for alumina, magnesia and beryllia from 1000 to 1800°C. Journ. Amer. Ceram. Soc., 1954, 37, No. 2, part II.

12. Shakhtin, D. M., I. I. Vishnevskiĭ, Opredelenie teploprovodnosti ogneuporov v vakuume (Determination of thermal conductivity of refractories in vacuum). Zavodskaya laboratoriya, 1957, 23, No. 8.

13. Taylor, R. E., Thermal conductivity and expansion of beryllia at high-temperatures. Journ. Amer. Ceram. Soc., 1962, 45, No. 6.

14. Reiswig, R. D., Thermal conductivity of UO_2 to 2100°C. Journ. Amer. Ceram. Soc., 1961, 44, No. 1.

15. Jamilson, I., A. W. Lawson, High-temperature heat conductivity of some metal oxides. Journ. Appl. Phys., 1958, 29, No. 9.

16. Whitemore, D. H., Exitation process in ceramics and anomalous increase in thermal conductivity at elevated temperatures. Journ. Appl. Phys., 1960, 31, No. 6.

17. McGleland, I. D. and E. H. Zems, Thermal conductivity of magnesia from 1030 to 1880°C. Journ. Amer. Ceram. Soc., 1960, 43, No. 1.

18. Ioffe, A. V., A. F. Ioffe, Teploprovodnost' tverdykh rastvorov poluprovodnikov (Thermal conductivity of solid solutions of semiconductors). Fizika tverdovo tela, 1960, II, No. 5.

19. Kingery, W. D., Thermal conductivity, XIV, Conductivity of multicomponent systems. Journ. Amer. Ceram. Soc., 1959, 42, No. 12.

20. Kopeĭkin, V. A., D. N. Poluboyarinov, O fazovom sostave vysokoglinozemistoĭ keramiki (On the phase composition of high-alumina content ceramics). Ogneupory, 1960, No. 12.

21. Kukolev, G. V., Khimiya kremniya i fiziko-khimiya silikatov (Chemistry of silicone and physical chemistry of silicates). Gosstroĭizdat, 1952.

22. Kaĭnarskiĭ, I. S., E. V. Degtyareva, Sb. trudov UNII-Ogneuporov, 1958, No. 2.

23. Bezborodov, M. A., N. D. Zav'yalov, A. A. Sokolov, ZhTF, 1935, No. 6.

24. Kurlyankin, Keramika i steklo, 1936, No. 2.

25. Berman, R., P. G. Klemens, F. E. Simon, T. M. Fry, Nature, 1950, 166.

26. Kingery, W. D., Thermal conductivity, XI, Determination of conductivity of Al_2O_3 by spherical envelope and cylinder methods. Journ. Amer. Ceram. Soc., 1954, 37, No. 2, part II.

27. Devyatkova, E. D., A. V. Petrov, I. A. Smirnov, B. Ya. Moĭzhes, Plavlenyĭ kvarts kak obraztsovyĭ material pri izmerenii teploprovodnosti, 1960, II, No. 4.

28. Ratcliffe, E. H., Thermal conductivity of fund and crystalline quartz, Brit. Journ. Appl. Phys., 1959, 10, No. 1.

29. Wray, R. L., T. J. Connoly, Thermal conductivity of clear phased silica at high temperatures. Journ. Appl. Phys., 1959, 30, No. 11.

30. Lee, D. W. and W. D. Kingery, Radiation energy transfer and thermal conductivity of ceramic oxides. Journ. Amer: Ceram. Soc., 1960, 43, No. 11.

31. Chudnovskiĭ, A. F, Teplofizicheskie kharakteristiki dispersnykh materialov (Thermophysical characteristics of dispersed materials). Fizmatgiz, 1962.

32. Smoluchowski. Thermal conductivity of powders under reduced air pressures. International critical tables, II, 315.

33. Kaganer, M. G., L. I. Glebova, Teploprovodnost' izolyatsionnykh materialov pod vakuumom (Thermal conductivity of insulation materials under vacuum). Kislorod, 1959, No. 1.

34. Shakhlin, D. M., I. I. Vishnevskiĭ, Opredelenie teploprovodnosti ogneuporov v vakuume (Determination of thermal conductivity of refractories in vacuum). Zavodskaya laboratoriya, 1957, 23, No. 8.

35. Kumagai Naoiti, C., Ito Hidebumi. Mem. Coll. Sci. Univ. Kyoto, Ser., 1935, B22, No. 2 (RZhFiz., 1957, No. 6, 14063).

36. Shlykov, Yu. P., E. A. Ganin, Termicheskoe soprotivlenie kontakta (Thermal resistance of contact). Atomnaya energiya, 1960, 9, No. 6.

37. Shlykov, Yu. P., E. A. Ganin, N. B. Demkin, Issledovanie kontaktnogo teploobmena (Investigation of contact heat transfer). Teploenergetika, 1960, No. 6.

38. Shlykov, Yu. P., E. A. Ganin, Kontaktnyĭ teploobmen (Contact heat transfer). Gosenergoizdat, 1963.

39. Kolechkova, A. F., V. V. Goncharov, Teplovye svoĭstava magnezitovykh ogneuporov (Thermal properties of magnesite refractories). Ogneupory, 1955, No. 1.

40. Shtrauf, E. A., Molekulyarnaya fizika (Molecular physics). Gostekhizdat, 1949.

41. Sinel'nikov, N. N. , V. N. Filippovich, Adiabaticheskiĭ kalorimĕtr - pribov dlya odnovremennogo opredeleniya teploemkosti i teploprovodnosti (Adiabatic calorimeter: an instrument for simultaneous determination of heat capacity and thermal conductivity). ZhTF, 1958, 28, No. 1.

42. Wygant, I. F. , M. S. Crowley, Effects of high-conductivity gases on the thermal conductivity of insulating refractory concrete. Journ. Amer. Ceram. Soc. , 1958, 41, No. 5.

43. Russell, H. W. , Principles of heat flow in porous insulator. Journ. Amer. Ceram. Soc. , 1935, 18, No. 1.

44. Loeb, A. L. , Thermal conductivity, VIII, A theory of thermal conductivity of porous materials, Journ. Amer. Ceram. Soc. , 1954, 37, 2, part II.

45. Laubitz, M. J. , Thermal conductivity of powders. Canad. Journ. Phys. , 1959, 37, No. 7.

46. Pustovalov, V. V. , Opredelenie teploprovodnosti ogneuporov do 1200° metodom statsionarnogo teplovogo potoka (Determination of thermal conductivity of refractories up to 1200°C by the steady-state constant heat flow method). Ogneupory, 1959, No. 4.

47. Pustovalov, V. V. , Izmerenie teploprovodnosti ogneuporov do temperatury 1500°C (Measuring thermal conductivity of refractories up to a temperature of 1500°C). Sb. nauchnykh trudov UNIIOgneuporov (Coll. Sci. Works of UNIIOgneupory), 1960, vyp. 3 (50).

48. Pirogov, A. A. , V. V. Pustovalov, O teploizolyatsionnykh svoĭstvakh nekotorykh vysokoogneupornykh poroshkov (On thermal insulation properties of some highly refractory powders). Sb. nauchnykh trudov UNIIOgneuporov (Coll. Sci. Works of UNIIOgneupory), 1962, vyp. 6 (52).

49. Pustovalov, V. V., Metodika izmereniya koeffitsienta teploprovodnosti ogneuporov pri vysokikh temperaturakh (Method of measuring thermal conductivity at elevated temperatures). Zavodskaya laboratoriya, 1957, 23, No. 9.

50. Pustovalov, V. V. , O vysokotemperaturnykh (do 2400°C) opredeleniyakh v vakuume teploprovodnosti ogneupronykh

materialov (On high temperature determinations [up to 2400ºC] of thermal conductivity of refractory materials in vacuum). Sb. nauchnykh trudov UNIIOgneuporov (Coll. Sci. Works of UNIIOgneupory), 1961, vyp 5 (52).

51. Pustovalov, V. V. , O teploprovodnosti alyumosilikatnykh ogneuporov (On thermal conductivity of alumina-silicate refractories). Ogneupory, 1961, No. 8.

52. Pustovalov, V. V. , Izmenenie teploprovodnosti kvartsevogo stekla v protsesse kristallizatsii (Variation in thermal conductivity of quartz glass during the crystallization process). Steklo i keramika, 1960, No. 5.

53. Pustovalov, V. V. , Teploprovodnost' nekotorykh ogneupornykh materialov (Thermal conductivity of some refractory materials). Ogneupory, 1961, No. 7.

54. Pustovalov, V. V. , O vliyanii stepeni razrezheniya na effektivnuyu teploprovodnost' ogneupornoi keramiki (On the influence of evacuation on effective thermal conductivity of refractory ceramics). Inzh. -fiz. zhurnal, 1960, III, No. 10.

55. Pustovalov, V. V. , Teploprovodnost' ogneupornykh poroshkov i spechenoi keramiki (Thermal conductivity of refractory powders and baked ceramics). Steklo i keramika, 1961, No. 12.

National Aeronautics and Space Administration

WASHINGTON, D. C.   20546

OFFICIAL BUSINESS